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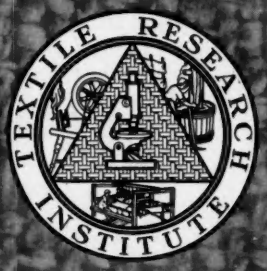


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TEXTILE RESEARCH JOURNAL

# Change of Address

All functions of the Publications Department of Textile Research Institute now conducted in New York City will be transferred to the Institute's offices in Princeton, New Jersey at the end of this year. This includes the editorial and subscriptions departments of Textile Research Journal. All manuscripts and communications which are likely to arrive subsequent to December 26 should be mailed to the address below.

The Institute's policy of maintaining the Publications Department as a separate operation is to be continued and the present high standard of the Journal will be maintained. All papers including those submitted by T.R.I. staff members are submitted to independent review. Members of T.R.I. staff serve as reviewers only when requested to do so by the authors. Julian S. Jacobs will continue as Editor-in-Chief of the Journal and Director of the Publications Department.

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TEXTILE RESEARCH JOURNAL

VOL. XXV, NO. 9 SEPTEMBER 1955

# A Study of Blended Woolen Structures[1]

## Part I: Statistics of the Ideal Random Blended Yarn

Myron J. Coplan and William G. Klein

THIS is the first in a series of reports on an experimental study of the effect of blending in woolen fabrics. The program is aimed at the improved utilization of wool in Navy fabrics. An extensive literature and field survey [4] which preceded the present work highlighted many of the problems and important considerations germane to the subject of blends, with particular reference to blends with wool.

The experimental program was initiated with an examination of the distribution of the fibers in a pedigreed series of wool-nylon and wool-viscose woolen yarns. Evaluation of the blend uniformity in these yarns is the subject of a subsequent report. This first report attempts to define the statistics pertinent to the problem of attaining blend uniformity in any ideal two-component yarn.

It is frequently stated as an axiom with reference to yarn regularity that the best that present processing machinery can do in the preparation of spun yarns is to arrange fiber ends in a random order. This limitation on the ability of machines is certainly no less applicable in the manufacture of blended yarns than in single-component yarns. In a blended yarn the effect of randomization of fiber ends leads to two kinds of irregularity.

First, of course, there is nonuniformity of total number of fibers per cross-section, which occurs in any spun staple yarn. The formulas applicable to this form of irregularity (i.e., the familiar weight nonuniformity of spun yarns) have been given in a number of places [2, 6, 9, 12].

The validity of the assumption that unlimited random distribution of weight along the length of a yarn represents the practical "ideal" has been questioned. Picard [11] and Vanden Abeele [15], both treating the problem in a general and rigorous mathematical fashion, formulate what is probably a more realistic picture. They take into account an upper limit to possible number of fibers in a cross-section, an upper limit which is not statistical but determined by the mechanical features of the process delivering the yarn. Further, there is a practical lower limit since, presumably, the existence of a continuous coherent strand requires that nowhere will there be fewer than a certain critical number of fibers in a cross-section. Finally, it is a reasonable assumption that the number of fibers in neighboring cross-sections will be highly correlated.

In the context of the general formulation given by these latter workers, the "random" yarn of Martindale is a simplified special case. At this point in the present discussion the simplification is not particularly disturbing and therefore the concept of an unrestrictedly "random yarn" will be pursued. Later, in the statistical development, the restrictions imposed by consideration of Vanden Abeele's formulation are considered.

Besides ordinary weight nonuniformity, in a blended yarn complete randomization of fibers leads to a second irregularity. As Lund [8] points out,

[1] Program supported by the United States Navy, Office of Naval Research and Bureau of Supplies and Accounts.

if one were to blend otherwise identical black and white fibers on present-day machinery the best possible blend would contain some grouping together of whites and also grouping together of blacks. Cox [1] states, in the same vein, "Even with a large number of doublings the best that can be expected is a random dispersion of colored and white fibers in the cross-section of the yarn, so that from time to time the surface fibers will be predominantly of one color." Cox was concerned with the statistical effect of mixing by doubling. Recently Lund [7] has treated the problem of blend "intimacy" in a limited theoretical fashion for carded yarns.

The necessity for an adequate general theory of "random" blending for carded yarns is illustrated by Townend [14] during a study of woolen carding. The investigation involved visual examination of woolen slivers delivered from a card which was fed equal parts of red-dyed and blue-dyed 70's wool. A 50–50 blend by weight was "carded on a 3–2 card (Scotch feed). . . . During carding it become apparent from the appearance of the condensed slivers that the fibers were not thoroughly mixed. . . . Instead of the fibers being uniformly distributed, the sliver was made up of distinct patches of blue and red fibers." A number of repeat experiments were made in which card settings were changed, processing steps modified, and even the lengths of the fibers reduced to $\frac{3}{8}$ of an inch. "Again the slivers were uneven in color. It is therefore reasonable to ask whether slivers produced on other carding machines are similarly uneven in the distribution of component fibers. Examination of the fibers in commercial slivers shows that they too are unevenly distributed, but industrially the blend does not consist of violent contrasting colors, so the fault is not discernible."

Townend examines in some detail the mechanism of the carding operation and observes that in many respects it does not provide the best conditions for breaking down locks of wool into single-fiber elements nor does it provide the best chance for the fibers of one lock to be mixed with the fibers of another. The conditions will be of importance later, but for the present Townend's philosophy is of interest. He is satisfied that "even if every group of fibers could be wholly disentangled and thoroughly mixed with every other group of fibers, so that there was an equal chance of either color being presented by the card we cannot hope to obtain a perfectly mixed sliver. There is a limit to the mixing capacity of the card as long as it does not select fibers but presents them randomly."

It seems likely, then, that blend imperfection is not only generally observed but must be accepted as an unavoidable consequence of current manufacturing techniques. This evidently applies to wool with wool blends as well as to blends of other fibers. The notion of "perfect blending" then, even under optimum realistic processing conditions, should properly be abandoned and an analysis intending to describe the lack of homogeneity in a blended yarn should employ statistical criteria. These are to be developed from the proposition that the result of complete mixing would be randomness. It will be understood, however, that these criteria represent the limits of blend homogeneity obtainable if all processes and reactions provide for random assorting of the fibers. Any other processing method with the "intelligence" to deal selectively with fibers and to sort them in other than a random fashion will require other analytical techniques. At this time, however, there seems to be no such machine or procedure and therefore the ideal still revolves about the basic principle of randomness.

## Simple Weight Irregularity

### 1. *The Ideal Case*

Imagine an inexhaustible supply of rice grains in a bin. One dips his hand into this bin and grasps a handful of rice. The handful is thrown up against a vertical rectangular screen having, let us say, $M$ equivalent holes in it, each large enough to pass only one grain of rice at a time. Some of the grains pass through the holes, and some fall back. The grasping and tossing of a handful of rice against the screen is repeated indefinitely. Count the total number of grains $T$ ($M$ represents the maximum possible value of $T$) passed at each tossing; for any one toss let this value be $T_i$.

Assume, first, that the screen is stationary and that the passage or nonpassage of any particular grain through the screen is determined by purely random factors. In this case, then, except for the upper limit of $M$ set by the available number of holes in the screen, the total number of grains passed per throwing is essentially determined by a

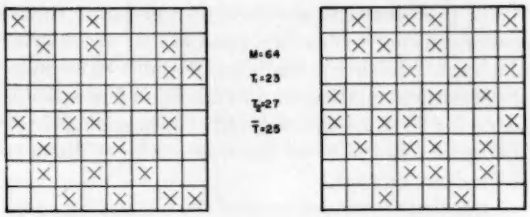


**Fig. 1.** Illustration of random screening with upper limit, $M$.

variety of random interactions among the rice grains and between these and the obstructing wires of the screen. Let $P$ be the probability of any hole passing a grain in a toss. The average number of grains passed per tossing, $\bar{T}$, will then be $PM$.

It can be shown that if $M$ is large enough and $\bar{T}$ is greater than 5 [5], the standard deviation of $T$ is very closely determined by

$$\sigma_T = \sqrt{MPQ} \tag{1}$$

where

$M$ = Maximum possible number that can pass at one time

$T_i$ = Total number that pass at any one time

$\bar{T}$ = Average number that pass at a time

$P = \bar{T}/M$

$Q = 1 - P$

The situation may be illustrated as in Figure 2, where each x'd box represents a rice grain passing through the screen, and the empty boxes represent a screen hole through which no grain passed at a given tossing.

Now, consider a singles woolen yarn which is produced in a conventional fashion. The viewpoints of Picard and Vanden Abeele seem altogether reasonable and we assume, with them, that there is an upper limit, $M$, to the number of fibers which a delivery can emit at any one time. In the simplest case involving this upper limit and where all other factors that quantitatively influence the emission of fibers at the spinning frame are randomly operative, let cross-sections of yarn be taken at intervals greater than a fiber length. The number of fibers at any given section will be $T_i$ and the average number $\bar{T}$. As in the rice-screen analogy,

$$\sigma_T = \sqrt{\bar{T}\left(1 - \frac{\bar{T}}{M}\right)} = \sqrt{\bar{T}Q} \tag{2}$$

This is essentially the equation developed by Vanden Abeele to represent a standard for the ideal yarn (roving or sliver) where the variability of number of fibers per section is "due to a completely random repartition of the fibers." It differs only in regard to the modifying term under the radical from the classical equation

$$\sigma_T = \sqrt{\bar{T}} \tag{3}$$

developed by Martindale, and used very extensively. In the development of his equations, Martindale makes a different set of assumptions, where the equivalent of $M$ in equations (1) and (2) becomes infinitely large; i.e., there is no reasonable upper limit set on the possible number of fibers per section. It is readily seen that as $M \to \infty$ equations (2) and (3) are the same.

## 2. *Some Causes of Departure from Ideality*

Return again to the analogy of the rice passing through the screen. Let the screen be fixed on trunions and be rocked randomly back and forth so that it successively presents more and less favorable aspects of the holes to the approaching grains of rice being tossed at it. The values of $T$ now are dependent not only on the random interaction of the grains on each other and the wire screen, but also on the angle of inclination of the whole screen which simultaneously effects the passage of rice through all the screen holes. This would correspond to a periodic systematic influence that simultaneously effects the passage of *all* the fibers being delivered at a given instant. In Vanden Abeele's analysis this type of phenomenon enters as a Lexis component in the general yarn irregularity equation. Both Martindale [10] and Thorndike [12, 13] provide many suggestions for the actual processing causes of this type of irregularity.

It would serve little purpose here to develop any further, by means of analogy, the Vanden Abeele equation for variation of total fibers per cross-section in a yarn. The form of the equation adapted from him, however, for a yarn which (a) is subject to the upper limit restriction and (b) is essentially random, but (c) suffers from a systematic influence of the sort described by the analogy is

$$\sigma_T = \sqrt{\bar{T}Q + M(M-1)\sigma_l^2} \tag{4}$$

Where

$M$, $\bar{T}$, and $Q$ are as previously defined
$\sigma_l^2$ = A variance characteristic of the periodic influence

Obviously, the second term under the radical (the Lexis component) may be very influential in determining the ultimate variability of $T$ but very little is known at this time about the absolute values involved.

Another concept pertaining to a cause of non-ideal irregularity is felt to be equally realistic for the woolen yarns under study and perhaps applicable even more generally. Imagine that the grains of rice in the bin have been slightly dampened so that they tend to adhere in little clumps or clusters. Also reconstruct the screen through which the rice is to pass so that it has fewer but larger holes.

Let

$C$ = Average number of grains per cluster
$M/C$ = Number of holes in screen
$\bar{T}/C$ = Average number of clusters passed per toss
$P = \bar{T}/C \div M/C = \bar{T}/M$, as before
$Q = 1 - P$, as before
$\sigma_C$ = Standard deviation of the number of clusters which pass per toss

For purely random screening, from equation (1),

$$\sigma_C = \sqrt{(M/C)PQ} \tag{5}$$

$$= \sqrt{\bar{T}Q/C} \tag{6}$$

The number of individual grains will be $C$ times the number of clusters and therefore

$$\sigma_T = C\sqrt{\bar{T}Q/C} = \sqrt{C\bar{T}Q} \tag{7}$$

It will be seen that equation (7) differs from equation (3) by two multiplying factors. The value $Q$ never exceeds 1 but it will differ from yarn to yarn and should be dependent on a variety of factors such as yarn size, fiber length, draft, etc.

Vanden Abeele gives the value $Q$ as about 0.5 for some otherwise unspecified yarn. The clustering factor, $C$, can be 1 or anything greater. In any event, if the systematic delivery upset described in equation (4) is not taken into account, the product $CQ$ must exceed 1 in order to account for irregularities where $\sigma_T > \sqrt{\bar{T}}$.

The problem most pertinent to blend uniformity, however, is not to describe gross weight irregularity of a yarn. Rather it would be desirable to examine the statistical relationships to ascertain a reasonable value for $C$, since this will indicate how effectively the mixing has reduced the feed-stocks of fibers to single-fiber elements.

Equation (7), which ignores the Lexis component in equation (4), rearranges to

$$C = \frac{\sigma_T^2}{\bar{T}Q} \tag{8}$$

which, of course, cannot be solved without knowledge of the value for $Q$.

If the clustering effect is introduced into equation (4), which does take into consideration the additional realistic influences of systematic delivery upsets, it can be shown that

$$C = \frac{\sigma_T^2 - M^2\sigma_l^2}{\bar{T}Q - M\sigma_l^2} \tag{9}$$

Solution of equation (9) is altogether impossible since both $Q$ and $M$ [directly related by $Q = (1 - T/M)$] are not known and certainly no information is at hand regarding $\sigma_l$. Fortunately, in blended yarns another statistical approach may be used to extract values for a coefficient of clustering, as will be developed in later sections.

The notion of clustering in woolen-type yarn is probably quite valid. Townend [14], for example, considers it extremely unlikely that commercial woolen carding will break down wool locks into single-fiber elements and that quite large aggregates of fibers may easily operate together as a spinning unit. It is also obvious when one tries to tease apart a woolen yarn that many fibers are so tangled together that they more than likely had passed through the entire processing as a group. Cox [1] refers also to the possible inability of a processing system to break down original groupings into single fibers, particularly in "coarse" systems other than in worsted drawing. In subsequent calculations statistical evidence will be given that "average clusters" of between two and four fibers per cluster exist. This is considered reasonable.

A very similar "coefficient of fiber association" is calculated by Grishin [3] to account for part of the irregularity of nonblended cotton yarns. While this latter author's assumptions and mathematical development are rather more complex than those of

the present ones, his results are in remarkably good agreement with the findings for the wool blend yarns to be discussed in Part II. His method of calculating the coefficient as used for self-blends appears to be limited to drafted yarns where ingoing and outcoming products are available for analysis.

### Blend Irregularity along the Yarn

1. *The Ideal Case*

Consider again the rice-screen analogy, but this time the inexhaustible bin has been loaded with a blend of two kinds of rice, say white and brown. The bin contents have been thoroughly mixed to randomize completely the individual grains. Ignore, for the present, any clustering; each grain is independent of all others. Now repeat the tossing of handfuls from this bin through the screen; as before, let

$T_i$ = Total of grains to pass in any one toss
$\bar{T}$ = Average total number of grains to pass per toss
$p$ = Number proportion of white grains in the whole blend
$1 - p = q$ = Number proportion of brown grains in the whole blend

If the screen does not selectively reject one of the two kinds of grains (i.e., the blend discharged from the screen is subject only to random effects), then

$\bar{W} = p\bar{T}$ = Average number of white grains to pass per toss
$\bar{B} = q\bar{T}$ = Average number of brown grains to pass per toss

For a fixed value of $T$, say $T_i$, the expected variability of $W$, $S_W$, will follow the same general (approximate) statistical relationship as was expressed for the variability of $T$ where there was a fixed $M$ (equation 1):

$$S_{W_i} = \sqrt{T_i pq} \tag{10}$$

Again, for this approximation to hold, $T$ must be fairly large (say in excess of 50) and $Tp > 5$. These conditions are met throughout the current work, where $T_i$ never falls below 150 and $p$ never falls below 0.15.

It should be evident, since $W_i + B_i = T_i$, that for every increment of $W_i$ there must be an equal decrement of $B_i$ (the number of brown grains per toss), and it therefore follows that equation (10) expresses the variability of both components for any given value of $T$.

$$S_{B_i} = \sqrt{T_i pq} \tag{10a}$$

For the problems that follow, the "internal variation" of $W$ must be treated for the case where $T$ also varies and an average value of $\bar{S}_W$ must be used. To derive this value, let $f_1$, $f_2$, etc. = frequencies of occurrence of values $T_1$, $T_2$, etc.

$$\begin{aligned} \bar{S}_W &= \sqrt{f_1 {S_{W1}}^2 + f_2 {S_{W2}}^2 + \cdots / \Sigma f} \\ &= \sqrt{f_1 T_1 pq + f_2 T_2 pq + \cdots / \Sigma f} \end{aligned} \tag{11}$$

and therefore

$$\bar{S}_W = S_{\bar{W}} = \sqrt{\bar{T} pq} \tag{12}$$

Consider the grains of rice passing through the screen at any one toss to be equivalent to the number of fiber cross-sections counted at any one yarn cross-section. The variability characteristics of the number of fiber sections per yarn cross-section will follow the same principles as apply to the number of rice grains per toss so long as these sections are taken at a sufficiently remote distance (one fiber length or more) so that each section contains substantially a new group of fibers.

Before attacking the problem of blend variation in a yarn, some aspects of the foregoing analogy should be clarified. It must be realized that the average number of whole fibers that may be counted in some finite length of yarn will differ from the average number of fiber sections that will be counted at a yarn cross-section, since the former depends on the length of yarn taken and the fiber length distribution. Obviously, in two yarns of given denier, one composed of short fibers will exhibit a greater number of whole fibers in a given length than one composed of longer fibers.

This effect does not bear on the present statistical problem since in both yarns there will be the same average number of fiber cross-sections per yarn cross-section. Even though the probability of finding a particular fiber at a given yarn section depends on its length, the probability of finding a given *kind* of fiber at a yarn cross-section depends on the *sum* of lengths of that kind of fiber.

Thus, take all the wool fibers in a particular sample of the blend and lay them down end-to-end.

Then do likewise with all the remaining nonwool fibers in the particular sample. Let the length of the string of single wool fibers be $p$ units long; the length of the string of nonwool fibers will be $q$ units long. The blend proportions can be defined in terms of these summative lengths as

$$p/q = \frac{\sum_{i=1}^{w} L_i}{\sum_{j=1}^{a} L_j} \qquad (13)$$

Where

$L_i$ = Length of the $i$th wool fiber
$L_j$ = Length of the $j$th fiber of other kinds
$w$ = Total number of wool fibers
$a$ = Total number of other fibers

Now, let the entire sampling of wool and other fibers be assembled into a randomly mixed yarn. It will be seen that the probability of finding a wool fiber cross-section at a yarn cross-section is $p$ when the probability of finding a cross-section of the other kind of fiber is $q$. These two probabilities are, therefore,

$$p = \bar{W}/\bar{T}$$
$$q = \bar{A}/\bar{T}$$

Where

$\bar{T}$ = Average total number of fibers per section
$\bar{W}$ = Average number of wool fibers per section
$\bar{A}$ = Average number of other fibers per section

If the blend variability conforms to the ideal defined as completely random, the variation in composition at a section with $T_i$ total fibers can be predicted. This variation, in terms of the number fraction of wool fibers per yarn cross-section, is the variation of the ratio $W/T$. Since, however, for any given value $T$, say $T_i$, only the numerator $W_i$ varies, then the standard deviation of this ratio for a given value of $T$ is

$$\sigma_i \text{ (Blend proportion)} = S_{W_i}/T_i = \sqrt{pq/T_i} \qquad (14)$$

The mean proportion will, of course, be $p$ and therefore for 99% of sections containing $T_i$ fibers the proportion of wool fibers will fall between

$$p \pm 2.58\ (S_{W_i}/T_i) \qquad \text{or} \qquad p \pm 2.58\sqrt{pq/T_i}$$

Cox [1], by a somewhat different approach, perhaps more refined but nevertheless involving certain restrictive assumptions which are not necessarily valid in the present work, also presents an approximation for variability of blend proportion. It is interesting to compare his predictions with those arrived at through the foregoing formulation (see Table I).

**TABLE I. 99 Per Cent Limits for Proportion of *W* Fibers in a Section**

| Number of Fibers per Cross-Section ($T_i$) | 50–50 Blend ($p = q = 0.5$) | | 20–80 Blend ($p = 0.2; q = 0.8$) | |
|---|---|---|---|---|
| | Cox | M.J.C. | Cox | M.J.C. |
| 30 | 0.28, 0.72 | not applicable | 0.071, 0.45 | not applicable |
| 50 | 0.32, 0.68 | not applicable | 0.091, 0.38 | not applicable |
| 100 | 0.38, 0.62 | 0.37, 0.63 | 0.12, 0.32 | 0.10, 0.30 |
| 200 | 0.41, 0.59 | 0.42, 0.58 | 0.14, 0.28 | 0.13, 0.27 |

It is apparent that where the $T_i pq$ approximation is applicable it yields prediction values insignificantly different from those of Cox. Moreover, it is a statistical formulation amenable to other valuable manipulations, as will be indicated. In any event, one may conclude from the information of Table I that 99% of all sections taken in an ideal random blended yarn composed in the aggregate of equal lengths of two kinds of fiber will exhibit a ratio of number of fibers at a section varying between 40–60 and 60–40, when there are as many as 150–200 fibers per section on the average.

### 2. *CV of Blend in the Ideal Case*

In practice it may often seem desirable to deal with blend uniformity in terms of CV of composition as determined by examining a number of discrete samplings out of a population of yarn. For example, a yarn may be divided into a number of small lengths and the wool and other fibers counted in each sampling or the weight proportions of each of the fiber types may be determined by some chemical analysis. The average number (or weight) percentage of wool would be determined and the variability among these samples also calculated. In the present work yarns were cross-sectioned and the fibers counted at each of several cross-sections.

Consider the case for CV of number concentration. The variation of blend proportion in numbers of wool fibers is actually the variation of the ratio $W_i/T_i$. Since, however, for every value of $T_i$ only the numerator $W_i$ varies, the standard deviation

of the blend proportion by number (i.e., the standard deviation of $W_i/T_i$) among sections containing $T_i$ total fibers will be, as indicated by equation (14),

$$\sigma_i \text{ (Wool conc., number)} = S_{Wi}/T_i = \sqrt{pq/T_i}$$

The CV of blend proportion of wool by number will be

$$\begin{aligned} CV_i \text{ (Wool conc., number)} &= 100\sqrt{(pq/T_i)} \div (\bar{W}/\bar{T}) \\ &= 100\sqrt{(pq/T_i)} \div p \\ &= 100\sqrt{q/p \cdot (1/T_i)} \end{aligned} \quad (15)$$

This will be the CV of blend concentration by number as found among cross-sections of equal total number of fibers. It is known, however, that all sections do not have the same total number of fibers. It might, at first, appear reasonable to employ $\bar{T}$ directly in equation (15). It can be shown, though, that

$$\frac{\Sigma \frac{1}{T}}{n} > \frac{1}{\bar{T}}$$

and that the higher the standard deviation of $T$, the greater the discrepancy.

In the general case the exact extent of the influence of total weight irregularity cannot be predicted, but it must be allowed for. Therefore, let the term $(1 + x)$ [1] represent the influence of yarn weight irregularity and then the general expression for CV of number concentration of wool fiber at cross-sections would be

$$\overline{CV} \text{ (Wool conc., number)} = \sqrt{q/p \cdot (1/T)(1 + x)} \quad (16)$$

Now, from equation (16) it can be shown that the CV of weight per cent concentration of wool at cross-sections will be

$$\overline{CV} \text{ \% wt. of wool} = 100\sqrt{\frac{\alpha}{\omega} \cdot \frac{1}{\bar{D}} (\alpha d_w + \omega d_a)(1 + x)} \quad (17)$$

Where

$\omega$ = Wt. fraction of wool in blend (e.g., 0.65 for 65% wool)

$\alpha$ = Wt. fraction of other fibers in blend = $1 - \omega$

$d_w$ = Average denier of wool fibers

$d_a$ = Average denier of other fibers

$\bar{D}$ = Average denier of yarn

The equivalent form, for the CV of weight per cent of nonwool fibers, will be

$$\overline{CV} \text{ \% wt. of nonwool fibers} = 100\sqrt{\frac{\omega}{\alpha} \frac{1}{\bar{D}} (\alpha d_w + \omega d_a)(1 + x)} \quad (18)$$

For convenience in further discussion, equation (18) may be rewritten in a different form as follows:

$$\overline{CV}\% \text{ wt. of nonwool fiber} = 100\sqrt{\frac{d_w}{\bar{D}} \frac{\omega}{\alpha}\left(\alpha + \omega \frac{d_a}{d_w}\right)(1 + x)} \quad (19)$$

Equation (19) would be applied in a practical case as follows. Imagine that a woolen yarn of 1000 den is customarily spun from 5 den wool fibers (about 64's). The equivalent yarn is to be spun of blends of 25 and 50% nylon. There is a choice of 1 or 5 den nylon staple. What is the expected effect of average blend composition on blend uniformity? What advantage to blend uniformity can be anticipated by proper selection of the nylon staple?

$$\frac{d_w}{\bar{D}} = 0.005 \text{ throughout}$$

$$\frac{\omega}{\alpha} = 1 \text{ or } 3 \text{ for } 50\text{–}50 \text{ or } 75\text{–}25$$

$$\frac{d_a}{d_w} = 1/5 \text{ or } 1 \text{ for 1 den or 5 den nylon}$$

The calculated CV's of blend for the ideal yarns would therefore be

50% nylon, 1 den nylon = $100\sqrt{0.003\ (1 + x)}$

50% nylon, 5 den nylon = $100\sqrt{0.005\ (1 + x)}$

25% nylon, 1 den nylon = $100\sqrt{0.006\ (1 + x)}$

25% nylon, 5 den nylon = $100\sqrt{0.015\ (1 + x)}$

Assuming that the gross weight irregularity of all four yarns is the same (i.e., $x$ is constant throughout), it is apparent that the finer fibers will yield the better blend uniformity for a given average

[1] It can be shown that the magnitude of $(1+x)$ rarely exceeds 1.05 and for most normal yarns would be nearer 1.02.

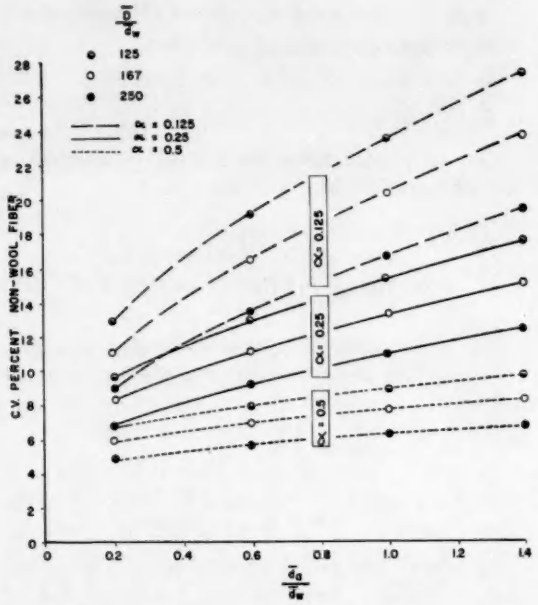


**Fig. 2.** The effect of fiber denier ratio on blend irregularity.

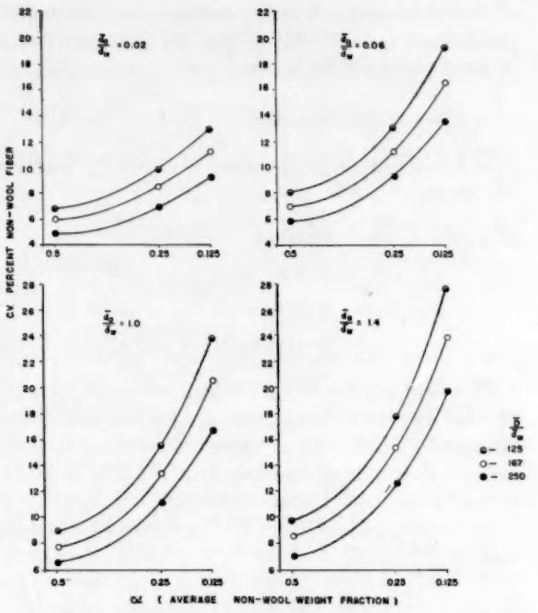


**Fig. 3.** The effect of average blend composition on blend irregularity.

concentration; also, the higher average concentration will provide the lower blend variation.

A graphical summary of the foregoing equation is given in Figures 2 and 3. In Figure 2 the effect of varying the ratio of deniers is shown for three families of curves (50%, 25% and 12.5%, fiber $A$). In each family there is a plot for the case where the average yarn denier is 125, 167, and 250 times the average wool fiber denier (i.e., $\bar{d}w/\bar{D} = 0.008$, 0.006, 0.004). Figure 3 simply replots this same information showing $\alpha$, the average wt. fraction of nonwool fiber as the independent variable.

The graphs and sample calculations point up several things. First, it is apparent that use of the CV of per cent composition as a criterion of the efficiency of a blending operation is extremely treacherous unless all the pertinent factors are considered. Apparent improvements in CV can be accomplished in several ways without there being a real change in the degree of blend randomness. For example, if a mill is examining a variety of process operations to determine the system which provides the most uniform blended yarn, it must compare strictly comparable yarns only, viz.: equal in (1) average blend composition, $\alpha$; (2) in total weight irregularity, $(1 + x)$; (3) in average yarn weight, $\bar{D}$; and composed of the same fiber deniers, $d_w$ and $d_a$.

Secondly, from the practical point of view, better weight dispersion of a minor blend component can be achieved by increasing its proportion in the blend, reducing its average fiber denier, improving overall weight irregularity of the yarn, and increasing average yarn denier.

### 3. *Relationship of W and T*

Two separate types of irregularity that arise out of random distribution of fibers have been considered. The first concerns simply the variability of $T$, the total number of fibers per section of yarn.

The second concerns the variability of $W$ from section to section having the same value of $T$. Total variation of $W$ (the number of wool fibers per cross-section) must take account of the two variations simultaneously.

By analysis of variance, where the blend composition is random and $T$ is also varying, the overall section to section variability of $W$ can be found from:

$$\sigma_W^2 = p^2\sigma_T^2 + \bar{S}_W^2 \quad (20)$$

Where

$\sigma_W^2$ = Overall variance of number of wool fibers per section

$\sigma_T^2$ = Variance of total number of fibers per section

$\bar{S}_W^2$ = Average internal variance for wool fibers

$p = \bar{W}/\bar{T}$

Whence

$$\sigma_W = (\sqrt{\bar{W}^2\sigma_T^2/\bar{T}^2}) + \bar{T}pq \quad (21)$$

In the concept of the ideal blended yarn, then, where variation in total number of fibers is governed by equation (1) and variation in blend is governed by equation (12)

$$\sigma_W = \bar{W}\sqrt{(MPQ/\bar{T}^2) + (\bar{T}pq/\bar{W}^2)} \quad (22)$$

$$= \bar{W}\sqrt{(Q/\bar{T}) + (q/\bar{T}p)}$$

$$= \sqrt{\bar{W}}\sqrt{(\bar{W}Q/\bar{T}) + (\bar{W}q/\bar{T}p)}$$

$$= \sqrt{\bar{W}}\sqrt{pQ + q} \quad (23)$$

$$\sigma_N = \sqrt{\bar{N}}\sqrt{qQ + p} \quad (24)$$

Lund [13], assuming that in the ideal blended yarn the classical Martindale equation (3) applied to both variability of individual components in the blend and the total number of fibers, states, in our present terminology:

$$\sigma_T = \sqrt{\bar{T}} \quad (3)$$

$$\sigma_W = \sqrt{\bar{W}} \quad (25)$$

$$\sigma_N = \sqrt{\bar{N}} \quad (26)$$

It would be proper to combine the variabilities of $W$ and $N$ in this case according to

$$\sigma_T^2 = \sigma_W^2 + \sigma_N^2 \quad (27)$$

because not merely does $\bar{T} = \bar{W} + \bar{N}$, but since no restriction is put on $T_i$, the variabilities of $W$ and $N$ are mutually independent.

In the more realistic ideal case, where $M$ sets an upper limit on $T_i$, $W_i$ and $N_i$ are not mutually independent. Equations (23) and (24) may be more nearly valid than equations (25) and (26), but it still would not be correct to combine them through (27). This can be demonstrated as follows from equations (23) and (24):

$$\sigma_W^2 + \sigma_N^2 = \bar{W}(pQ + q) + \bar{N}(qQ + p) \quad (28)$$

Substitute

$$\bar{W} = \bar{T}p$$

$$\bar{N} = \bar{T}q$$

$$q = 1 - p$$

and rearrange equation (28) to

$$\sigma_W^2 + \sigma_N^2 = \bar{T}[Q + (1 - Q)(2p - 2p^2)] \quad (29)$$

It will be seen that the right side of equation (29) cannot be equated with $\sigma_T^2$ as is called for in equation (27). This is so since, by definition,

$$\sigma_T^2 = \bar{T}Q$$

and in equation (29) both $Q$ and $p$ are smaller than 1, which requires that

$$\bar{T}Q < \bar{T}[Q + (1 - Q)(2p - 2p^2)]$$

Hence, for the ideal case defined herein,

$$\sigma_T^2 < \sigma_W^2 + \sigma_N^2$$

It is obvious here again, as in the earlier discussion of equation (3), that if one assumed no upper limit to the possible number of fibers per cross-section (either total or blend component) then $Q$ approaches 1 as $M \to \infty$ and Lund's idealization becomes compatible with the present. Equation (23) reduces to (25) since $p + q = 1$, and the right-hand side of equation (29) reduces to $\bar{T}$, thereby justifying the use of (27).

## Departure from Blend Ideality

### 1. *Index of Blend Irregularity*

Data to be presented in a subsequent report indicate that the practical cases of some wool-nylon and wool-viscose yarns do not conform quantitatively with the foregoing idealizations. One would like to establish a quantitative basis for assessing the extent to which a yarn does differ from the ideal. One possible approach is to treat the question as a simple linear correlation problem.

Let the total number of fibers per section, $T$, vary as it will, due to whatever causes may be operative. If there is an established blend proportion, $p$, then there should be a correlation of $T$ with $W$ or a regression line whose equation is $W_i = pT_i$. A perfect blend would yield a correlation coefficient $r = 1.0$.

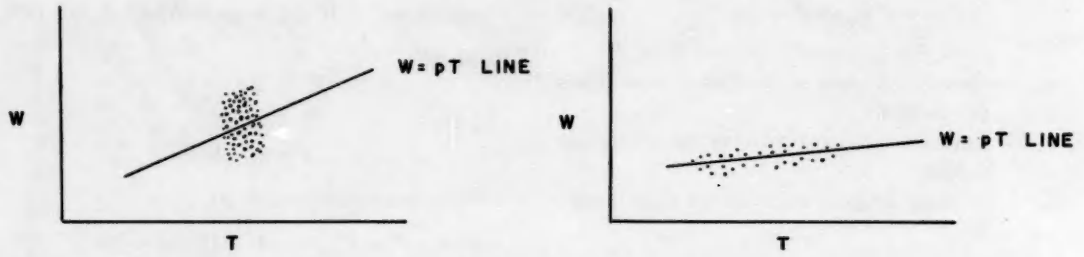


**Fig. 4.** Illustration of two cases where correlation of $W$ and $T$ may appear poor while blend conforms to the ideal: *a* (left), very uniform yarn weight; *b* (right), low concentration of one component.

An ideally random blended yarn should still show a dependence of $W$ on $T$, but $r$ will be less than 1.0 since perfect correspondence between $W_i$ and $PT_i$ is not expected. The reduced value of $r$ can be calculated from the general equation

$$r = \sqrt{1-\bar{S}_W^2/\sigma_W^2} \qquad (30)$$

The expression $\bar{S}_W^2/\sigma_W^2$ is known as the coefficient of alienation [16]. $\bar{S}_W$ is the standard error of estimate of $W$ for given values of $T$, and $\sigma_W$ is the standard deviation of $W$.

The theoretical standard error of estimate for $W$ is

$$\bar{S}_W = \sqrt{\bar{T}pq}$$

and the theoretical total dispersion of $W$ is, from equation (21),

$$\sigma_W = \bar{W}\sqrt{CV_T^2 + (\bar{T}pq/\bar{W}^2)}$$

Here the actual value of $CV_T$ is to be used, since no stipulation is made that total weight irregularity conform to an ideal, but simply that whatever the total number of fibers at a cross-section, the blend should vary according to the ideal.

The coefficient of alienation then, for the ideal so defined, is

$$\frac{\bar{S}_W^2}{\sigma_W^2} = \frac{\bar{T}pq}{\bar{W}^2\left(CV_T^2 + \dfrac{\bar{T}pq}{\bar{W}^2}\right)} \qquad (31)$$

which reduces to

$$\bar{S}_W^2/\sigma_W^2 = \bar{T}pq/p^2\sigma_T^2 + \bar{T}pq \quad \text{(theoretical)} \qquad (32)$$

The actual coefficient of alienation will employ

$$\bar{S}_W = \sqrt{\frac{\sum(pT_i - W_i)^2}{n}} \quad \text{(actual)}$$

and

$$\sigma_W \quad \text{(actual)}$$

and therefore is

$$\frac{\bar{S}_W^2}{\sigma_W^2} = \frac{\sum(pT_i - W_i)^2}{n\sigma_W^2} \quad \text{(actual)} \qquad (33)$$

An index to express the extent to which a given blended yarn departs from the condition of ideal randomness may use either the difference or the quotient of equations (33) and (32). Examination of these equations, however, reveals that such a practice is not necessarily useful. It will be seen that as $\sigma_T$ becomes small, that is, as the yarn weight uniformity is improved, the theoretical coefficient of alienation approaches 1, and therefore a good correlation of $W$ and $T$ may not be expected. This is illustrated in Figure 4*a*, where the blend composition is not out of order, but the yarn is quite uniform in total number of fibers per section. In this case equation (33) also approaches unity since the numerator and denominator are both almost entirely dependent on the blend uniformity and $\bar{S}_W$ approaches equality with $\sigma_W$.

A second case exists where the blend is very dilute (i.e., where $p$ is quite small), and again equation (32) approaches a value of 1. This is illustrated by Figure 4*b*, where the dispersion of $T$ may be high and the dependence of $W$ on $T$ may conform to the ideal but an index based on coefficient of alienation or, by the same token, the coefficient of correlation would be insensitive.

A much more sensitive index, and one that does not depend at all on how the weight irregularity itself varies, can be developed by using essentially only the numerators of equations (32) and (33). Thus, consider a section in which $T_i$ total and $W_i$

wool fibers are found. The expected limit of error of estimate for the theoretical random blend is $\sqrt{T_i pq}$ and the found error will be $(pT_i - W_i)$. Now, if these two items are compared as in

Index of Blend Irregularity

$$= \sqrt{\frac{1}{M}\sum \frac{(pT_i - W_i)^2}{T_i pq}} \quad (34)$$

then one gets directly a measure of the extent to which the blend deviates from expected randomness. In fact, the index so calculated is a normalized standard deviation which measures the degree of blend homogeneity where 0 is perfection and where 1 is randomness. An index of 1.3 has the physical meaning that the blend suffers from causative factors which increase its inhomogeneity by 30% above what can be expected from a purely random process operating on single-fiber elements.

2. *Clustering Coefficient*

We can return now to the previously mentioned likelihood of fiber "clusters" occurring during spinning. As before, in equations (5) and (11), let

$C$ = Average number of fibers per cluster
$T_i/C$ = Total number of clusters at a section
$W_i/C$ = Number of wool clusters at a section
$p$ = Proportion of wool clusters in the total blend of clusters
$q$ = $(1 - p)$ as before

Replace $W_i$ and $T_i$ with $W_i/C$ and $T_i/C$. Now, if the blend consists of a purely random dispersion of fiber clusters instead of single fiber elements, but otherwise conforms with the general ideal, then the I.B.I. for the clusters will be 1. Substituting in equation (34) and squaring,

$$1 = \frac{1}{M}\sum \frac{(pT_i - W_i/C)^2}{T_i pq/C} \quad (35)$$

which yields

$$C = \frac{\sum (pT_i - W_i)^2/(T_i pq)}{n} \quad (36)$$

In arriving at equation (36), it has been tacitly assumed that the average number of fibers per cluster is the same for both components of the blend and therefore for the yarn as a whole. It has also been assumed that the clusters are homogeneous, not comixtures. The accuracy of the first assumption can be checked, as a first approximation, by examining the values of $C$ found for a series of blends of increasing wool content. For two such series the clustering coefficient does not shift markedly with blend so the assumption seems reasonable. The validity of the second assumption cannot be readily checked, but it is also believed reasonable in view of the small values for $C$ that were found, namely, 2–4. Besides, the tangling together of a wool with a nylon fiber presupposes previous separation into single-fiber elements and therefore, by definition, prescribes a condition of random intermingling.

A method of determining the clustering of each fiber component individually can be developed as follows:

Let

$\bar{G}$ = Average total number of all clusters per section
$p'$ = Proportion of wool clusters in blend
$q'$ = Proportion of nylon clusters in blend
$c$ = Average number of wool fibers per cluster
$k$ = Average number of nylon fibers per cluster

$$\bar{S}_G = \sqrt{\bar{G}p'q'} \quad (37)$$

But

$$\bar{G}p' = \bar{W}/c = \bar{T}p/c$$

$$q' = \frac{\bar{N}}{k} \div \left(\frac{\bar{N}}{k} + \frac{\bar{W}}{c}\right) = 1 + \frac{1}{\frac{\bar{W}}{\bar{N}}(k/c)}$$

Also

$$\bar{W}/\bar{N} = p/q \qquad \text{and therefore}$$

$$\bar{S}_G = \sqrt{\frac{\bar{T}p}{c + (pk/q)}} = \sqrt{\bar{T}pq/(qc + pk)} \quad (38)$$

Again, however, the variability of number of *fibers* will be $c$ times equation (38) for wool and $k$ times equation (38) for nylon.

$$\bar{S}_W = \sqrt{c^2(\bar{T}pq/qc + pk)} \quad (39)$$

$$\bar{S}_N = \sqrt{k^2(\bar{T}pq/qc + pk)} \quad (40)$$

But the real values of $\bar{S}_W$ and $\bar{S}_N$ are found from

$$\sigma_W^2 = p^2 \cdot \sigma T^2 + \bar{S}_W^2 \quad (41)$$

$$\sigma_N^2 = q^2 \cdot \sigma T^2 + \bar{S}_N^2 \quad (42)$$

Using experimental values for $\sigma_T$, $\sigma_W$, $\sigma_N$, $T$, $p$, and $q$, and dividing equation (39) by equation (40) and (41) by (42), the ratio $c/k$ can be solved from

$$(\sigma_W^2 - p^2\sigma_T^2)/(\sigma_N^2 - q^2\sigma_T^2) = c^2/k^2 \quad (43)$$

With the ratio $c/k$ and its inverse $k/c$, it is possible to determine $c$ and $k$ individually from the combined and rearranged forms of equations (39)–(42).

$$c = (q + pk/c)(\sigma_W^2 - p^2\sigma_T^2/\bar{T}pq) \quad (44)$$

$$k = (p + qc/k)(\sigma_N^2 - q^2\sigma_T^2/\bar{T}pq) \quad (45)$$

The analytical method defined by equations (44) and (45) has been applied to the series of yarns in two ways. First, the variables of fiber count, blend proportion, etc. were determined from entire cross-sections of yarn. This provides a measure of the extent to which fibers "ran together" along the length of the yarn. The method was also applied to samplings *within* cross-sections, as will be described in Part II, to give some idea of the extent to which fibers remained "paired" within given cross-sections.

## Summary

1. A method of predicting the variability of blend proportion along the yarn has been developed.

2. A general expression for CV of per cent composition was developed and the influence of fiber weight, yarn weight, blend composition, and yarn weight irregularity were pointed out.

3. For CV of wt. per cent of the minor component in a blend, the ideal yarn shows better homogeneity with (a) finer fiber deniers, (b) higher wt. fraction of the minor component, (c) coarser yarn, and (d) better gross weight uniformity of the yarn.

4. In view of (3), caution must be exercised when comparing two blended yarns to be sure that the principal controlling factors in blend regularity are strictly comparable.

5. An objective criterion of blend randomness, the Index of Blend Irregularity, was developed.

6. An approximation of the degree of fiber clustering was derived by manipulation of the I.B.I.

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## Addendum

Since the completion of the foregoing manuscript, an article by Hampson and Onions (*Journal of the Textile Institute*, **46**, T377) on essentially the same subject has been published. The present authors wish to take cognizance of this work and comment on it.

While at first there appear to be certain resemblances between the results of the present work and that of Hampson and Onions, there is a fundamental difference in theoretical approach that warrants some emphasis. Actually, the same disparity in statistical philosophy exists between our approach and that of Hampson and Onions as was alluded to on p. 744 in discussing the work of Lund.

Whereas these other workers in posing the problems of blend regularity set no upper limit on the possible number of fibers per cross-section, the present work is based on the assumption that a finite limit does actually exist and formulates the problem in that light. The two approaches may be contrasted as follows:

a. In the present work, the total number of fibers to be found at a cross-section, $T$, is a variable whose limits are controlled by the process of spinning. For this case, the standard deviation of total number of fibers for the "ideal" yarn is given by equation (1)

$$\sigma_T = \sqrt{MPQ} = \sqrt{\bar{T}Q}$$

where

$$MP = \bar{T}$$
$$P + Q = 1, \quad Q < 1$$

In the approach of Hampson and Onions and of Lund, the Poisson distribution is employed, leading to

$$\sigma_T = \sqrt{\bar{T}}$$

b. In the present work, a binary blended yarn is *not* construed statistically as being composed of two singles yarns plied together. The two fiber types do not operate entirely independently of one another, but rather the numbers of each kind that may be found at a section are each statistically dependent on the total number of fibers that occur at that section.

In this framework, the expected number of "white" fibers at a section is given by $pT_i$ with a standard deviation $\sqrt{pqT_i}$, where

$T_i$ = Actual total number of fibers at a section

$p$ = Number proportion of "whites" in the blend

$q = 1 - p$ = Number proportion of "blacks" in the blend

In effect, the contrasting statistical approach postulates that each of the fiber types is spinning as a singles yarn and that the blend composition at sections in the combined yarn is equivalent to that obtained by plying. This interpretation of Hampson and Onions' approach may be illustrated by their assumption that the expected number of white fibers at any section will be $p\bar{T}$ with a Poisson distribution about this value, having as its approximate standard deviation $\sigma_W = \sqrt{p\bar{T}}$.

From this it can be reasoned that the distribution of $T$ is essentially governed by

$$\sigma_T^2 = \sigma_W^2 + \sigma_B^2$$

where

$\sigma_T$ = Standard deviation of total number of fibers

$\sigma_W$ = Standard deviation of number of whites

$\sigma_B$ = Standard deviation of number of blacks

which is for a 50-50 blend equivalent to the "law of doubling,"

$$\sigma_{\text{Ply}} = \sigma_{\text{Single}} \sqrt{2}$$

where

2 = Number of plies

Such an approach leads to the irreconcilable situation that 50 blacks and 50 whites at a section containing a total of 100 fibers is an improper blend for a 50-50 yarn whose expected total number of fibers per cross-section is 150, because the expected number of whites is

$$p\bar{T} = 75;$$

the variation of whites is

$$\sigma_W = \sqrt{p\bar{T}} = 8.7$$

and

$$p\bar{T} - 2\sigma_W = 75\text{-}17 = 58.$$

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# International Symposium

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# The Reaction between Cellulose and Formaldehyde

## Influence on the Mechanical Properties of Viscose Rayon Fibers

**E. Marianne Kärrholm**

*Swedish Institute for Textile Research*

**Abstract**

The moduli at bending, torsion, and stretching were determined for viscose rayon fiber with different amounts of formaldehyde. A maximum value of all three moduli was obtained at about 5% fixed formaldehyde. The properties at cyclic loading were also investigated.

The results indicate that the number of crosslinks are increased at increasing amounts of fixed formaldehyde up to 5%. At higher values, the length of the crosslinks is increased.

Formaldehyde polymers, soluble in sodium sulfite, may cause considerable changes in the mechanical properties.

WHEN treating cellulose with formaldehyde at elevated temperatures and in the presence of an acid catalyst methylene bridges were supposed to be formed between two glucose residues of the cellulose as early as 1929 [10]. Later this reaction and, especially, the results of the reaction have been the object of a great number of investigations [3, 4, 5, 13].

The actual chemical structure of the product has recently been studied by Wagner and Pacsu [12], and they state that one molecule of formaldehyde reacts with two hydroxyl groups of the glucose residues of cellulose. They have investigated cellulose containing up to 6.5% covalently linked formaldehyde. We were first trying to study the chemical structure of the reaction product by using the tosylation-iodination technique together with periodate oxidation. The cellulose, however, became very inreactive after treatment with formaldehyde. Even swelling in sodium hydroxide and replacing the hydroxide with water and the water with an organic solvent did not lead to quantitative conversion reactions for cellulose containing more than 0.5% fixed formaldehyde.

The experiments were then concentrated on the determination of the changes in the mechanical properties caused by the formaldehyde treatment. This was made both in order to get information on the structure of the product and because a change in the mechanical properties of the fibers is the main purpose of the formaldehyde treatment.

The moduli at bending, torsion, and stretching were determined for rayon fibers with different amounts of formaldehyde. The bending and torsion experiments were performed at very low stresses, so that the elastic properties were the same after these experiments as before. The stretching experiments, however, were performed until break. It was thus possible to determine these moduli on the same fiber, if the fiber was subjected to bending, torsion, and stretching in the order mentioned. Besides these constants, the properties of the formaldehyde-treated fiber were determined after repeated loading and unloading. These results were used to calculate the elastic performance coefficient (E.P.C.) as described by Hamburger [6] and could also be used for division of the total strain into immediate elastic deflection, delayed elastic deflection, and permanent set.

Formaldehyde polymers are practically always formed when cellulose is treated with formaldehyde. These polymers are, however, soluble in sodium sulfite or in sodium hydroxide; most of them also, in boiling water.

The formaldehyde remaining in the cellulose after treatment with sodium sulfite is designated as "fixed"

TABLE I.

| Concentration of Formaldehyde in the Bath | Time and Temperature at Condensation | Amount of Formaldehyde in the Fiber (%) Before Treatment with Sodium Sulfite | Amount of Formaldehyde in the Fiber (%) After Treatment with Sodium Sulfite |
|---|---|---|---|
| 4.0 | 15 min at 110°C | 3.3 | 2.5 |
| 8.2 | | 7.2 | 5.2 |
| 12.0 | | 11.6 | 6.9 |
| 16.2 | | 14.2 | 9.2 |

formaldehyde in this investigation, whereas soluble formaldehyde means formaldehyde or formaldehyde polymers, soluble in sodium sulfite.

The investigation of the mechanical properties has been made both on fibers containing only fixed formaldehyde and on fibers containing both fixed and soluble formaldehyde.

## Material

Untwisted yarn of viscose rayon silk, consisting of 18 model filaments with circular cross-section (diameter = 40 $\mu$) was used for the experiments [7].

The formaldehyde solutions were made from paraformaldehyde by boiling with water under reflux until solution. The concentrations used were: 4%, 8%, 12%, and 16% formaldehyde. Ammonium chloride was used as a catalyst (0.21 g/l, *p*H 3.1–2.4). Ten samples of the yarn of 8 mg each were fastened to perspex plates. Two samples were soaked in each of the four formaldehyde solutions and the remaining two samples in a blank solution. The time of immersion was 5 min. The excess solution was removed by squeezing between blotting papers. The samples were immediately dried and condensed in one step at 110°C for 15 min. Temperature measurements with a termistor coupled to a recorder showed that 2 or 3 min were sufficient for the wet samples to dry and reach 110°C. One sample from each treatment was soaked in sodium sulfite solution (1 *M*) overnight for solution of the formaldehyde polymers formed.

The formaldehyde content of the fibers was determined by a colorimetric micromethod using the violet compound formed between formaldehyde and chromotropic acid. The method by Boyd and Logan [1] gave bad reproducibility, whereas a sufficient accuracy was obtained with the method described by Kleinert and Srepel [9]. The amount of formaldehyde in the fibers after treatment is given in Table I.

TABLE II.

| Fixed Formaldehyde (%) | Bending Modulus $\times 10^{-8}$ gf/cm² | Fixed+Soluble Formaldehyde (%) | Bending Modulus $\times 10^{-8}$ gf/cm² |
|---|---|---|---|
| Control | 1.00 | Control | 1.05 |
| 2.5 | 1.23 | 3.3 | 1.23 |
| 5.3 | 1.28 | 7.2 | 1.42 |
| 6.9 | 1.16 | 11.6 | 1.61 |
| 9.3 | 1.14 | 14.2 | 1.35 |

The confidence limits = $\pm 0.057 \times 10^{-8}$ gf/cm² (Confidence coefficient = 0.95).

## Elastic Constants

The moduli at bending, torsion, and stretching were determined on the same fiber and for 10 fibers of each treatment. This means that in total 2 groups of 50 fibers each were tested. The sequence between all 50 fibers in each group was randomized. The confidence limits were determined for all fibers in the group at a confidence coefficient of 0.95.

## Bending Modulus

The bending modulus was determined with the resonance frequency method [7]. As the fibers had

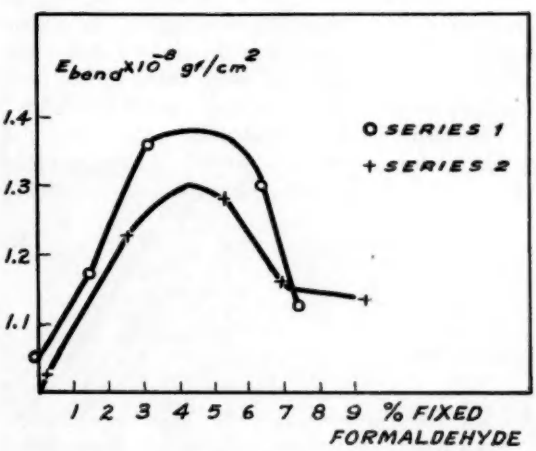


**Fig. 1.** Bending modulus of viscose rayon fibers as a function of the amount of fixed formaldehyde in the fiber.

**TABLE III.**

| Fixed Formaldehyde (%) | Torsion Modulus $\times 10^{-7}$ gf/cm² | Fixed+Soluble Formaldehyde (%) | Torsion Modulus $\times 10^{-7}$ gf/cm² |
|---|---|---|---|
| Control | 1.66 | Control | 1.57 |
| 2.5 | 2.09 | 3.3 | 1.91 |
| 5.2 | 2.25 | 7.2 | 2.38 |
| 6.9 | 2.00 | 11.6 | 2.82 |
| 9.2 | 1.84 | 14.2 | 2.08 |

Confidence limits = $\pm 0.16 \times 10^{-7}$ gf/cm² (Confidence coefficient = 0.95).

circular cross-sections, the diameter could be measured microscopically. A fiber length of about 2 cm was used, and the reasonance frequency obtained was 35–50 cycles/sec. The maximum stress in the fiber was less than $10^4$ gf/cm². The result is given in Table II.

The bending modulus passes a maximum at about 5% fixed formaldehyde (series 2 of Figure 1) analogous to a preceding experiment (series 1 of Figure 1). When soluble formaldehyde is also present the maximum value is obtained at about 11% formaldehyde.

### Torsion Modulus

The torsion modulus was determined with a modified torsion pendulum described by the author together with Nordhammar and Friberg (8).

The determination was performed as follows: After measuring the bending modulus, both ends of the fiber were fastened to small perspex plates and the time of oscillation was determined according to the method described in the above paper. At a fiber length of 1.5 cm a time of oscillation of 7–8 sec was obtained. The maximum shear stress in the fiber has been calculated to be about $5 \times 10^3$ gf/cm².

The result is given in Table III.

The torsion modulus also passes a maximum value at about 5% fixed formaldehyde. When soluble formaldehyde is also present, the maximum value is obtained at about 11% formaldehyde, analogous to the values of the bending modulus.

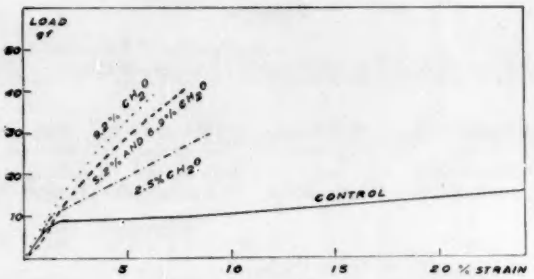


**Fig. 2.** Load-strain diagrams of formaldehyde-treated viscose rayon fibers. The amounts of formaldehyde refer to fixed formaldehyde.

### Stretching Modulus (Young's Modulus)

The same fibers used for the determination of the torsion modulus were placed with their perspex plates in the clamp of the Instron Tensile Tester. The first part of the stress-strain curve was recorded. A rate of elongation of 18% per minute was used and the specimen length was about 1.5 cm.

On the stress-strain curves obtained, the tangential modulus was drawn at a total load on the fiber of 1.25 gf, 2.5 gf, and 5 gf (1 gf corresponds to a strain of about $10^5$ gf/cm² for the fibers used).

The result is given in Table IV.

From this table is seen that Young's modulus at the lowest strain is independent of the amount of formaldehyde in the fiber. At larger stresses the modulus has a flat maximum at 3–5% fixed formaldehyde; when also soluble formaldehyde is present the maximum is obtained between 7–11% formaldehyde.

The change in the general characteristics of the stress-strain diagram after formaldehyde treatment is shown in Figure 2. The diagrams were obtained

**TABLE IV.**

| Fixed Formaldehyde (%) | Young's Modulus $\times 10^{-8}$ gf/cm² at a Load of | | | Fixed + Soluble Formaldehyde (%) | Young's Modulus $\times 10^{-8}$ gf/cm² at a Load of | | |
|---|---|---|---|---|---|---|---|
| | 1.25 gf | 2.5 gf | 5 gf | | 1.25 gf | 2.5 gf | 5 gf |
| Control | 0.55 | 0.65 | 0.71 | Control | 0.53 | 0.62 | 0.64 |
| 2.5 | 0.53 | 0.80 | 0.92 | 3.3 | 0.51 | 0.71 | 0.80 |
| 5.2 | 0.58 | 0.78 | 0.90 | 7.2 | 0.50 | 0.88 | 1.06 |
| 6.9 | 0.43 | 0.68 | 0.79 | 11.6 | 0.54 | 0.87 | 1.08 |
| 9.2 | 0.52 | 0.74 | 0.80 | 14.2 | 0.57 | 0.79 | 0.91 |

Confidence limits = $\pm 0.068 \times 10^{-8}$ gf/cm².

in the same way as described above although other fibers were used for this determination. As could be expected, the breaking strain is decreased after formaldehyde treatment, and the yield point gradually disappears. But at the same time there is a considerable gain in breaking stress, which is two to three times higher than for untreated fibers at formaldehyde contents of 2 to 9%.

### Mechanical Properties at Cyclic Loading

Fibers from the same treatments as described above were subjected to cyclic loading until completely mechanically conditioned (10 cycles).

The experiments were performed at three conditioning loads, corresponding to 1%, 3%, and 5% elongation of the fiber, respectively. On account of the large difference in the elongation at break of the treated and untreated fibers a strain of 5% corresponds to about 85% of the elongation at break for the treated fibers, but only to 25% for the untreated fibers.

The cyclic loading was made with an Instron Tensile Tester, using a gage length of 1.6 cm and a rate of extension of 18% per minute.

From the curves obtained, the elastic performance coefficient was determined according to the method described by Hamburger [6]. The result is given in Figure 3 for fibers with only fixed formaldehyde. When also soluble formaldehyde is present, a small increase in the values of the E.P.C. was obtained. (The largest increase compared to fibers with only fixed formaldehyde was 7% and referred to the fibers with 11.6% formaldehyde). For untreated fibers the E.P.C. decreases with increasing strain, but at 5% fixed formaldehyde in the fiber the E.P.C. is independent of the strain. When the amount of fixed formaldehyde is increased above 5%, this does not influence E.P.C.

The immediate and delayed elastic recovery and permanent set properties of the fibers were calculated from the same curves.

The fully conditioned cycle (the 10th) was used to determine the immediate and delayed elastic recovery, instead of the first and second cycle as described by Susich and Backer [11]. The principles for the calculation are seen from Figure 4. The Instron Tensile Tester was working continuously, after each loading returning to the original distance between the clamps. The time elapsing between each cycle then became about 15 sec. The slack in the fiber at the beginning of the test was large enough to make the time between the cycles rather independent of the amount of strain.

From Figure 5*a* and *b* it is seen that the immediate elastic deflection is increased and the permanent set decreased by the formaldehyde treatment, whereas the delayed elastic deflection only undergoes smaller changes. This is in accordance with the results in a recently published investigation on the elastic properties of urea-formaldehyde and melamine-formaldehyde treated cellulose [2]. When the fiber contains at least 5% fixed formaldehyde, the recovery properties are rather independent of the value of the total strain, which is, however, not the case when resins are also present.

Furthermore, almost the same diagram is obtained

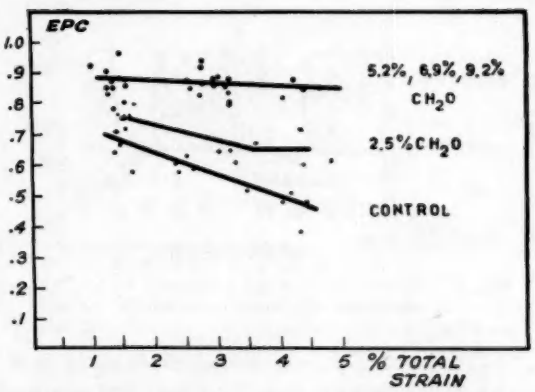


**Fig. 3.** Elastic performance coefficient of formaldehyde-treated viscose rayon fibers at different strains. The amounts of formaldehyde refer to fixed formaldehyde.

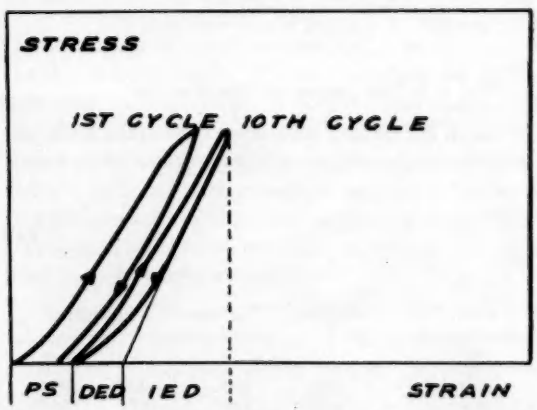


**Fig. 4.** The figure shows the principles for the calculation of immediate elastic recovery (I. E. D.), delayed elastic recovery (D. E. D.), and permanent set (P. S.).

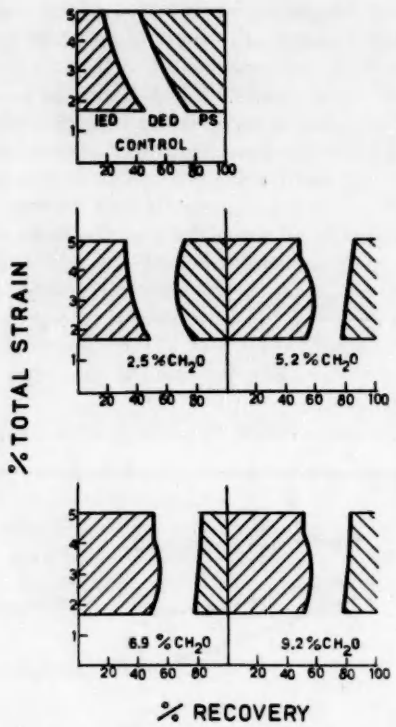


**Fig. 5a.** Elastic recovery and permanent set for fibers containing only fixed formaldehyde.

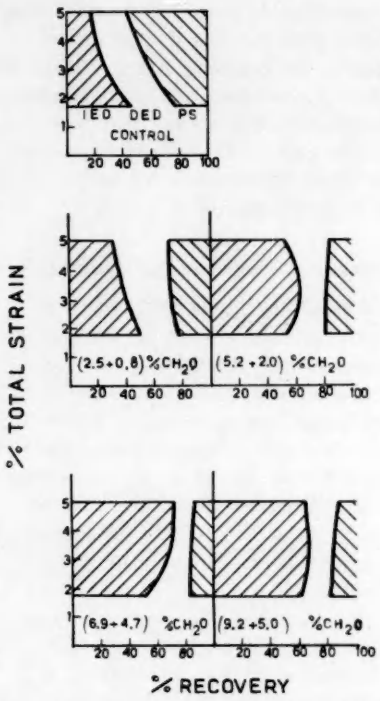


**Fig. 5b.** Elastic recovery and permanent set for fibers containing both fixed and soluble formaldehyde.

at 5.2, 6.9, and 9.2% fixed formaldehyde in the fiber, which is in agreement with the E.P.C. diagram.

At 6.9 and 9.2% fixed formaldehyde the soluble formaldehyde causes a considerable increase in immediate elastic recovery, mainly at the expense of the amount of delayed elastic recovery.

### Discussion of the Results

The bending and torsion moduli were both obtained from dynamic experiments (although at a very low frequency for the last), whereas a quasi-static method was used for the stretching modulus. A direct comparison between these moduli is therefore of little interest, and, instead, the relative moduli have been calculated, i.e., $E/E_o \times 100$, where $E_o$ is the modulus for the untreated fibers. Table V gives the values of these relative moduli and in Figure 6 they are plotted against the amount of fixed formaldehyde in the fiber, as well as for the fibers containing both fixed and soluble formaldehyde.

From the diagram is obtained: (1) All three moduli pass a maximum value when the amount of for-

**TABLE V.**

| Fixed Formaldehyde (%) | Relative Moduli at Bending | Torsion | Stretching 2.5 gf | Stretching 5 gf | Fixed + Soluble Formaldehyde (%) | Relative moduli at Bending | Torsion | Stretching 2.5 gf | Stretching 5 gf |
|---|---|---|---|---|---|---|---|---|---|
| Control | 100 | 100 | 100 | 100 | Control | 100 | 100 | 100 | 100 |
| 2.5 | 120 | 129 | 126 | 136 | 3.3 | 120 | 118 | 112 | 118.5 |
| 5.2 | 125 | 139 | 123 | 133 | 7.2 | 138 | 147 | 138.5 | 157 |
| 6.9 | 113 | 123.5 | 107 | 117 | 11.6 | 157 | 174 | 137 | 160 |
| 9.2 | 111 | 114 | 116 | 118.5 | 14.2 | 131 | 128.5 | 124 | 135 |

maldehyde is increased; (2) The curves for the relative bending and torsion moduli are following each other both when only fixed formaldehyde is present and when the fibers contain soluble formaldehyde as well; and (3) The curves for the relative stratching moduli show a similar dependence on the amount of formaldehyde, although the maximum values are obtained at somewhat lower amounts of fixed formaldehyde. (The relative stretching moduli at 1.25 gf are not included in the diagram; they are independent of the amount of formaldehyde).

Supposing one molecule formaldehyde reacting with two hydroxyl groups in different glucose units gives a maximum amount of formaldehyde of $30 \times 100/2 \times 162 = 9.3\%$ in the fiber. When only the amorphous parts are reacting, the maximum amount becomes $0.60 \times 9.3 = 5.6\%$. This is about the same value as that corresponding to the maximum in bending and torsional moduli, when only fixed formaldehyde is present.

When all possible methylene bridges have been formed an excess of formaldehyde present at the reaction may increase the amount of fixed formaldehyde by forming either longer crosslinks between the hydroxyl groups including two or more formaldehyde molecules or polymeric formaldehyde enclosed between the crosslinks, so that it cannot be solved by sulfite solutions.

For the further treatment it is necessary to discuss briefly the possible reasons for obtaining changes in the elastic moduli of formaldehyde-treated fibers.

*The bending modulus* is increased if the "effective area" becomes larger. However, a change of the "effective area" is not probable, as then the stretching modulus should also increase. For small stresses the latter modulus is independent of the formaldehyde content, as shown above. (Table IV)

The shearing forces also may affect the deflections in bending. This can, however, not explain that the increase obtained is of about the same magnitude as the increase in torsion modulus.

The most probable reason for an increase in bending modulus seems to be that by crosslinking compressed molecules within the fiber obtain larger resistance against buckling. Similarly, the bending modulus is decreased when the length of these crosslinks is increased.

It can be shown that the *torsion modulus* is proportional to the number of crosslinks and to the inverse value of their length.

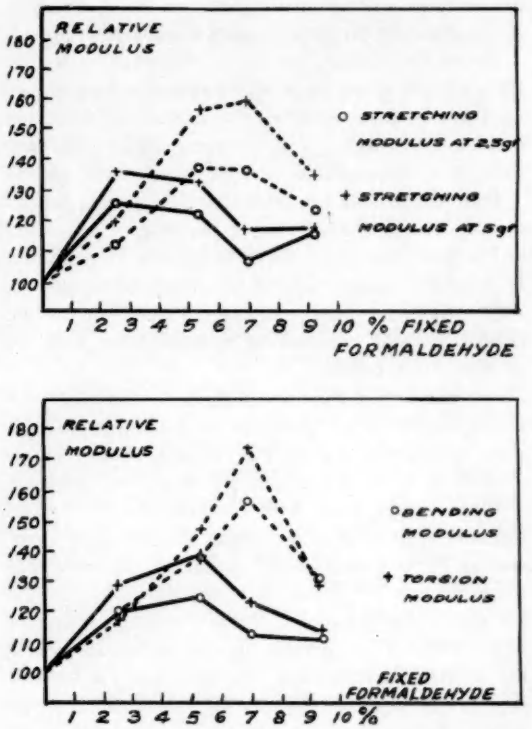


**Fig. 6.** The relative moduli at stretching, bending, and torsion as a function of the percentage *fixed* formaldehyde in the fibers. The full drawn curves refer to fibers containing only fixed formaldehyde. The dashed curves refer to fibers containing both fixed and soluble formaldehyde (as a function of only the fixed amount.)

When *stretching* the fibers, small loads cause a straightening of the molecules and a small increase in the valence angles. Forces perpendicular to the direction of the load are of minor importance. For larger loads, the stresses are transferred from one molecule to another by elements in the radial direction of the fiber. The crosslinks are then of the same importance as in bending and torsion, which explains the similarity between the relative stretching moduli and the other relative moduli.

Formaldehyde polymers between the cellulose chains may cause a breaking of the hydrogen bonds and thus a decrease of the moduli (analogous to water).

When formaldehyde polymers are present in larger concentration in the fiber, e.g., when the polymers

are situated mainly in the outer parts of the fiber, an increase in the moduli may be obtained.

From the dashed curves of Figure 6 it is seen that a slight decrease of the torsion and stretching modulus is obtained when the amount of fixed formaldehyde is below 4%, whereas above this value there is a considerable increase in all three moduli.

It is worthwhile to notice that 5% soluble formaldehyde causes a much larger increase in all moduli at 7% fixed formaldehyde than does the same amount of soluble formaldehyde at 9% fixed formaldehyde.

The following picture of the reaction between formaldehyde and cellulose is in accordance with the experimental results.

An increase of the concentration of formaldehyde at the condensation gives an increasing *number* of short crosslinks, giving rise to an increase in the moduli up to an amount of 5% fixed formaldehyde.

When the cellulose fiber contains about 7% fixed formaldehyde some of the crosslinks are longer, consisting of two or more formaldehyde molecules. From Figure 5 it is seen that the values of all moduli are decreasing between 5% and 7% fixed formaldehyde. The large increase in the moduli caused by the soluble formaldehyde can be explained by supposing the fiber to be very "inaccessible" and the soluble polymers mainly situated in the outer parts of the fiber.

If the condensation is performed at so high concentrations that about 9% fixed formaldehyde is obtained, crosslinks containing in average two formaldehyde molecules are probably formed, indicated by a further decrease of, especially, the torsion modulus. There will then be more space available in the interior of the fiber for the soluble formaldehyde polymers and the increase in the moduli caused by these polymers will not be as great as in the preceding case.

The experimental results do not exclude the possibility that smaller amounts of the fixed formaldehyde consist of formaldehyde polymers, enclosed between crosslinks and therefore insoluble.

## Acknowledgment

I feel deep gratitude to Dr. Gunnar Kärrholm for many stimulating discussions. I am also indebted to Professor Nils Gralén for valuable suggestions and interest in this investigation.

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# Use of the Schlieren Technique to Observe the Still Air Layer Above the Surface of Fabric Covering a Heated Flat Plate

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THE insulating properties of fabrics have often been associated with "still" air layers which exist over the surface of the fabric and add to its insulating value. This phenomenon was recognized early in the 19th century [3]. One of the early guarded-ring hot plates developed for testing fabrics [2] was provided with a hood so that the equipment could be operated in a room without disturbance of the "still" air layer by ambient air currents. Measurements of this air layer were made in the past by indirect methods [4]. To date the examination of the "still" air has been difficult since techniques for making this air visible have not been explored by investigators studying the thermal properties of fabrics. The Schlieren technique [7], whereby differences of air density can be made visible [1, 5], suggests the possibilities of photographing the air layer so that it can be accurately measured and its behavior observed in different environmental conditions.

This paper describes the preliminary experiment to demonstrate the feasibility of the application of the Schlieren technique. Further work, using motion pictures and color photographs, gives promise of explaining in greater detail the role of the "still" air layer in the insulation provided by a given fabric or combination of fabrics. A refinement of this technique to simulate the thermal condition of a human body should provide much valuable information. In fact, quantitative data regarding the limits of boundary layer, surface temperature, and heat-transfer rate are possible. Such data will be useful in designing better cold-weather ensembles by answering questions about the relative insulating value of different fibers and the most effective relative positions for rough or smooth surfaces to achieve maximum insulation.

The optics of the Schlieren apparatus are shown in the schematic diagram, Figure 1. Light is directed from point $L$ to a parabolic concave mirror, $K_1$, from which it is reflected in parallel rays to a similar mirror, $K_2$. This mirror is so slanted as to, in turn, reflect the beams to a camera, $P$, at the other side of the mirror system. A knife edge, $B$, is set at the focal point of the converging rays as they are reflected from the mirror, $K_2$, to the camera, $P$.

With this system, if the air density in the path of the parallel light is uniform, moving the knife edge, $B$, into the ray of light would produce a uniform darkening of the mirror surface. The specimen, $S$, which in this investigation consisted of a fabric covering a thermal plate, is positioned between the mirrors. As the heat flowing from the plate changes the air density in the light path, the camera, with the knife edge properly positioned in front of it, photographs the differences in density between the hot air directly along the fabric and the cooler ambient air. The hot-air layer appears on the photograph as a darkened area.

Figure 2 ($A$–$E$) shows photographs of 4 fabrics taken by the Schlieren technique at the David Taylor Model Basin of the U. S. Navy. A laboratory thermal plate was used. (No special apparatus was designed for the heat source.) The laboratory thermal plate was selected to fit in the space provided for this in the Schlieren system. The temperature of the thermal plate could be controlled at about 250°F. A check of its surface temperature indicated that the

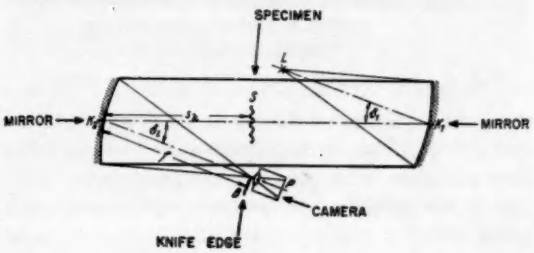


**Fig. 1.** Schematic diagram of apparatus for Schlieren photographs [7].

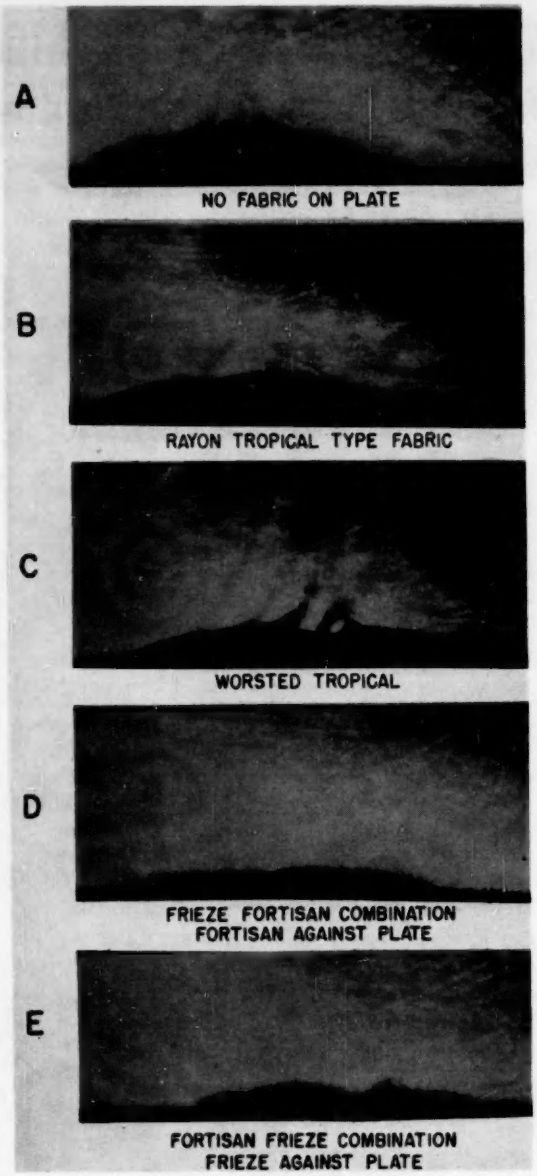


**Fig. 2.** Fabrics photographed by Schlieren method.

thermostat maintained the temperature between 235° and 260°F. The measurements were made on a hot July afternoon with the room temperature at 92°F. Thus, the effective temperature differential was about 160°F.

Four fabrics were tested in this exploratory investigation. Two were relatively thin fabrics of approximately equal weight and thickness but of different fiber content: a rayon tropical suiting and a tropical worsted. The third was wool frieze, a thick double-faced loop-pile fabric, and the fourth was 1.6-oz Fortisan lining fabric. The first two fabrics were tested separately; the third and fourth were tested as an ensemble, duplicating the standard liner formerly used in Army cold-weather clothing. The ensemble was tested in two ways, frieze side up and then Fortisan side up, to determine the effect on the height of the air layer of the radically different surfaces.

The thermal plate was placed in a 9-in. wind tunnel which formed an integral part of the Schlieren system used to make the measurements reported here. The gates of the tunnel were shut to provide a closed chamber.

Figure 2*A* shows the thermal plate at 250°F with no fabric covering. The boundary surface of the "still" air layer is clearly shown here. It extends 0.75 in. above the plate at the high point near the center.

With the rayon tropical sample on the plate, as shown in Figure 2*B*, the dark portion of the photograph, indicating the "still" air layer, measures 0.60 in., a loss in thickness of 0.15 in. Because of its smoothness, the rayon fabric can be considered similar in surface character to the thermal plate itself. It is assumed that, in general, for similar surfaces, the height of the air layer is directly related to the differences in temperature between the exposed surface and the ambient air. The difference between the height of the air layer over the bare plate and that over the rayon tropical fabric, therefore, indicates that the temperature at the surface of the fabric is less than that at the surface of the bare plate, and hence, that the fabric provides some degree of insulation. The less efficient the fabric is as an insulant, the higher the temperature at the fabric-air interface would be, and the thicker the air layer.

In Figure 2*C*, the plate was covered with tropical worsted fabric. After the photograph was taken, it was discovered that the fabric was not properly smoothed, and the photograph shows a break in the air layer where the fabric was not flat against the plate. Elsewhere, the air layer is 0.50 in. thick, slightly less than that over the rayon fabric. Further testing would be required to determine whether the difference between the two is significant. The disappearance of the air layer over the part of the

sample raised above the plate may be a substantiation of the value of an air space between the body and the fabric.

Figures 2*D* and 2*E* show the frieze-Fortisan ensemble. With frieze side up (Figure 2*D*), the air layer measured 0.30 in. With the Fortisan up (Figure 2*E*), the air layer thickness was 0.40 in. It should be borne in mind, however, that in the case of the frieze-Fortisan combination with the frieze side exposed to air the base line of the fabric is approximately 0.10 in. below the loop height. In the photograph, measurement of the air layer was made from the top of the loop to the outside boundary surface of the air layer. Here it is difficult to draw the line as to what constitutes the boundary layer of the fabric, the top of the loop or the top surface of the base fabric which holds the loop in place. It may well be that the two air layers' thicknesses are alike if the top of the base fabric is taken as a point for measurement. The fact remains, however, that the overall height of the assembly and air layer is lower when the frieze side is exposed to air than when the Fortisan side is so exposed. That is, for equivalent assemblies and test conditions, the air layer over a rough surface (such as frieze) is not as thick as the air layer over a smooth surface (such as the Fortisan fabric). It may be that further experiments with the technique will provide a clue to the possible value of napping and other treatments which roughen fabric surfaces for the purpose of improving insulation properties.

The data collected in this preliminary experiment are summarized in Table I. In all instances, the "still" air layer was seen to build up rapidly above the fabric. A slight circulation was noted, which was seen as a constant swirling action along the periphery of the heated layer. This circulating air was seen to rise to the top and center of the layer, where it then trailed off into the chamber atmosphere. A momentary blast, at 30 mph, when jetted across the fabric lowered the thickness of the air layer to the upper surface of the projecting fibers. When the jet was shut off, the layer rapidly regained its size and shape.

These few experiments have shown that the Schlieren method is well suited for investigating the thermal properties of the "still" air layer. Moreover, its applications can be categorized as follows:

TABLE I THICKNESS OF STILL AIR MASS OVER SURFACE OF HEATED FABRICS

| SAMPLE | ARRANGEMENT OF SAMPLE | WEIGHT OZ./SQ.YD. | THICKNESS OF FABRIC(") AT 0.01 PSI | THICKNESS OF FABRIC(") AT 0.1 PSI | THICKNESS OF AIR LAYER |
|---|---|---|---|---|---|
| NO FABRIC | HOT PLATE | — | — | — | 0.75 |
| RAYON TROPICAL | HOT PLATE | 6.7 | — | 0.020 | 0.60 |
| TROPICAL WORSTED | HOT PLATE | 6.7 | — | 0.020 | 0.50 |
| FRIEZE FORTISAN | HOT PLATE | 16.0<br>1.8 | 0.29<br>— | —<br>0.007 | 0.30 |
| FORTISAN FRIEZE | HOT PLATE | 1.8<br>16.0 | 0.29 | 0.007 | 0.40 |

*a.* A study of a "still" air layer around the surface of fabrics and fabric assemblies.

*b.* A quantitative evaluation of the temperature field defining the limits of the boundary layer, surface temperature, and heat-transfer rate.

These two categories for studying air layers offer a wide latitude for investigators working on thermal problems; for example, the study of conditions necessary for entrapping air in cold-weather clothing and dissipating the insulating air layer for hot-weather clothing. The design of garments can also be effectively studied from the standpoint of functional properties. Study can be made on scale models for the optimum design to accommodate subjects when at rest and also at high levels of activity.

Future plans using the Schlieren technique include the following series of studies:

*a.* Refinement of techniques to include temperature measurements by density measurements on the photographic plate. This will provide quantitative information not only on the boundary layer, but also on the measurement of the heat-transfer rate through the clothing system.

*b.* A study of individual fabrics, fabric layers in contact, and fabric layers artificially spaced at different thicknesses [6] to arrive at an optimum combination of fabric air for good insulation.

*c.* A pore-size study to determine hole size and shape in insulating material for retaining heat at low levels of motion and dissipating heat at higher levels of motion.

*d.* A study of the effect of air permeability of fabrics on the insulating properties of the garments.

### Acknowledgment

Appreciation is expressed for the continued interest shown in this program by Dr. S. J. Kennedy, Chief, Textile, Clothing, and Footwear Division, HQ Quartermaster Research and Development Command, Natick, Mass., and for the assistance and cooperation of the David Taylor Model Basin, Maryland, in obtaining the data described in this paper.

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# Thermal Insulation of Single and Multiple Layers of Fabrics[1,2]

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### Abstract

Thermal insulation, thickness, and volume of air per unit area of fabric have been determined for single and multiple layers of fabrics. A comparison of the thermal insulation and thickness values obtained by the actual measurement of multiple layers of fabrics to those obtained by adding the values of the individual fabrics involved has been made. In addition, thermal insulation data for the single and multiple layers of fabrics were plotted against the values for the other properties to show the relationships that exist.

INSULATING ability is of prime importance in the evaluation of fabrics used for winter outer wear in many regions. A perusal of the extensive literature on thermal insulation of fabrics and the properties associated with the prevention of heat losses shows that much has been published on the subject. A good review of this literature recently has been prepared by Morris [4].

A linear relation between thermal insulation and thickness measurements for single fabrics has been found by other workers [3, 5, 6, 7, 8]. They have shown that an empirical equation may be derived from thickness and thermal insulation measurements

[1] Paper No. 3323, Scientific Journal Series, Minnesota Agricultural Experiment Station.

[2] A report based on a section of a thesis submitted to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

**TABLE I. Descriptive Properties of Single Fabrics**

| Fabric Designation | Fiber Content | Woven or Knitted Structure | Fabric Count (yarns/in.) | | Fabric Weight per Sq Yd | Fabric Thickness 0.02 lb/in.² | Thermal Insulation |
|---|---|---|---|---|---|---|---|
| | | | W | F | (oz) | (in.) | (°C sec m²/cal) |
| *Coatings* | | | | | | | |
| All-wool worsted | 100% wool | Twill, even, 4-shaft | 112 | 51 | 9.70 | 0.0397 | 0.0937 |
| 40/60% worsted | 40% wool; 60% rayon and acetate | Twill, even, 4-shaft | 117 | 56 | 10.44 | 0.0361 | 0.0874 |
| 30/70% worsted | 30% wool; 70% rayon and acetate | Twill, even, 4-shaft | 105 | 52 | 9.94 | 0.0405 | 0.0874 |
| Light woolen | 100% wool | Twill, even, 4-shaft | 45 | 39 | 10.75 | 0.0866 | 0.1977 |
| Medium woolen | 100% wool | Twill, uneven, 3-shaft | 31 | 24 | 9.93 | 0.1074 | 0.2532 |
| Heavy woolen | 100% wool | Twill, uneven, 4-shaft | 28 | 28 | 11.62 | 0.1683 | 0.3889 |
| Dynel mixture | 85% rayon and acetate; 15% Dynel | Twill, even, 4-shaft | 56 | 39 | 8.68 | 0.0452 | 0.1047 |
| L. S. D. | | | 1 | 1 | 0.15 | 0.0014 | 0.0049 |
| *Heavy Linings* | | | | | | | |
| Rayon, quilted | Face: 100% acetate; bat: tissue paper and rayon; | Satin, 5-shaft | 196 | 66 | 18.01 | 0.3231 | 0.7201 |
| | back; 100% cotton | Plain | 43 | 37 | | | |
| Wool, quilted | Face: 100% acetate; bat: tissue paper and reprocessed wool; | Satin, 5-shaft | 189 | 75 | 13.13 | 0.2034 | 0.4475 |
| | back: 100% cotton | | 18 | 14 | | | |
| Metalized wool, quilted* | Face: 100% acetate; bat: wool; | Satin, 5-shaft | 232 | 75 | 9.33 | 0.1583 | 0.3291 |
| | back: 100% cotton | Plain | 18 | 14 | | | |
| 50% alpaca | 50% alpaca; 50% cotton | Filling knit | 19† | 14 | 12.43 | 0.0677 | 0.3466 |
| 75% alpaca | 75% alpaca; 25% cotton | Filling knit | 20† | 9 | 13.51 | 0.1865 | 0.4124 |
| L. S. D. | | | 2 | 2 | 0.51 | 0.0169 | 0.0117 |
| *Interlinings* | | | | | | | |
| Interlining | 100% wool | Plain | 13 | 13 | 4.97 | 0.0733 | 0.1599 |
| Zip-in interlining | 100% wool | Twill, even, 4-shaft | 26 | 24 | 8.15 | 0.0651 | 0.1501 |
| Significant Difference | | | ‡ | ‡ | ‡ | ‡ | ‡ |
| *Satin Linings* | | | | | | | |
| Satin lining | 100% acetate | Satin, 5-shaft | 226 | 74 | 4.26 | 0.0180 | 0.0396 |
| Metalize satin lining* | 100% acetate | Satin, 5-shaft | 212 | 61 | 3.85 | 0.0171 | 0.0366 |
| Significant Difference | | | ‡ | ‡ | ‡ | ‡ | ‡ |

* Back coated with resinated metal.
† Knitted fabrics: wale and coarse data given in warp and filling columns, respectively.
‡ Significant at the 1% level.

which will give an accurate estimate of the thermal insulation of a fabric and have concluded that thickness values should suffice for predicting thermal insulation under the same experimental conditions. It also is accepted generally that the air in the fabric, not the fiber, is largely responsible for its thermal insulating value.

Thermal insulation and other properties associated with heat losses through multiple layers of fabrics may be determined (1) approximately by adding the values for the individual materials or (2) by actually measuring the combinations of fabrics. When fabrics are combined, as in a coat, a thin layer of air can be enclosed between them which could contribute to the insulating ability of the combination. If this occurs, then the thermal insulating values of combinations of fabrics will be greater than the sum of the values for the single materials involved, and the equation calculated from thermal insulation and thickness measurements for single fabrics might not give accurate estimates for such multiple layers of fabrics.

In order to determine whether or not there is any measurable difference between values obtained by these two methods, the added and measured values for thermal insulation and thickness for various coatings, linings, interlinings, and combinations of these fabrics commonly found in ready-to-wear winter wear outer garments have been compared.

## Methods and Materials

Sixteen fabrics, varying in weight, construction, and fiber content, such as are used in ready-to-wear outer garments, were chosen for study. Data which describe the fabrics included in this study are given in Table I. The fabrics are divided into four groups, i.e., coatings, heavy linings, interlinings, and satin linings, depending upon their end-use in winter outer garments. The coatings were combined with the linings and lining combinations, as indicated in Table II, to form 31 different multiple layers of fabrics representing combinations commonly found in winter outer garments.

Standard methods of procedure were employed where such were applicable to the materials and the purpose of this investigation. In other cases a published method of procedure was modified to improve it for this purpose. All physical measurements, except that for volume of fiber, were made under standard atmospheric conditions (65% R. H. and 70°F, plus or minus 2% and 2°, respectively).

Thermal insulation determinations were made using a Fitch heat transfer apparatus [2] which had been modified to make it more suitable for fabric measurements. The modifications enable the heat source to be raised and lowered and the distance between it and the receiver to be set accurately. During the determinations the distance was adjusted so as to equal that of the measured thickness of the fabric sample at a pressure of 0.02 lb/in.$^2$, the heat source being maintained at 100° C plus or minus 1°C.

The volume of fiber in each of the 16 fabrics was measured with the Russell Volumeter, using carbon tetrachloride. The volume of air then was obtained by subtraction and the cubic centimeters of air per unit area of fabric were calculated from this value

**TABLE II. Mean Values for the Thermal Insulating Capacity of Combinations of Fabrics**
(Least significant difference for comparison of group means = 0.0174)

| Lining or Lining Combination | Coatings | | | | | | |
|---|---|---|---|---|---|---|---|
| | 100% Worsted | 40/60% Worsted | 30/70% Worsted | Light Woolen | Medium Woolen | Heavy Woolen | Dynel Mixture |
| | | | | (°C sec m$^2$/cal) | | | |
| 75% alpaca | 0.6137 | 0.5411 | 0.5927 | 0.7123 | | | 0.6220 |
| 50% alpaca | 0.5965 | 0.5787 | 0.5087 | 0.7178 | | | 0.6312 |
| Rayon, quilted | | | | 1.0586 | 1.1021 | 1.2059 | |
| Wool, quilted | | | | 0.8550 | 0.9598 | 0.9728 | |
| Metalized wool, quilted | | | | 0.6538 | 0.7595 | 0.9650 | |
| Interlining* | | | | 0.4666 | 0.4962 | 0.6451 | |
| Zip-in† | 0.3300 | 0.3258 | 0.3227 | 0.4831 | 0.5521 | 0.7109 | |
| Metalized satin | | | | 0.2590 | 0.3221 | 0.4469 | |

* Interlining, as used here, includes plain weave interlining plus satin lining.
† Zip-in lining, as used here, includes rayon satin plus twill weave zip-in interlining plus rayon satin.

**TABLE III. Mean Added Thermal Insulation Values for Multiple Layers of Fabrics**

| Lining or Lining Combination | Coatings | | | | | | |
|---|---|---|---|---|---|---|---|
| | 100% Worsted | 40/60% Worsted | 30/70% Worsted | Light Woolen | Medium Woolen | Heavy Woolen | Dynel Mixture |
| | | | | (°C sec m²/cal) | | | |
| 75% alpaca | 0.5061 | 0.4998 | 0.4998 | 0.6101 | | | 0.5171 |
| 50% alpaca | 0.4403 | 0.4340 | 0.4340 | 0.5443 | | | 0.4513 |
| Rayon, quilted | | | | 0.9178 | 0.9733 | 1.1090 | |
| Wool, quilted | | | | 0.6452 | 0.7007 | 0.8364 | |
| Metalized wool, quilted | | | | 0.5268 | 0.5823 | 0.7180 | |
| Interlining | | | | 0.3972 | 0.4527 | 0.5884 | |
| Zip-in | 0.3230 | 0.3167 | 0.3167 | 0.4270 | 0.4825 | 0.6182 | |
| Metalized satin | | | | 0.2343 | 0.2898 | 0.4255 | |

**TABLE IV. Mean Values for the Thickness of Combinations of Fabrics**

(Least significant difference for comparison of group means = 0.0105)

| Lining or Lining Combination | Coatings | | | | | | |
|---|---|---|---|---|---|---|---|
| | 100% Worsted | 40/60% Worsted | 30/70% Worsted | Light Woolen | Medium Woolen | Heavy Woolen | Dynel Mixture |
| | | | | (in.) | | | |
| 75% alpaca | 0.2454 | 0.2175 | 0.2404 | 0.2900 | | | 0.2523 |
| 50% alpaca | 0.2426 | 0.2366 | 0.2090 | 0.2916 | | | 0.2543 |
| Rayon, quilted | | | | 0.3917 | 0.4150 | 0.4400 | |
| Wool, quilted | | | | 0.3348 | 0.3653 | 0.3720 | |
| Metalized wool, quilted | | | | 0.2606 | 0.2973 | 0.3601 | |
| Interlining | | | | 0.1831 | 0.1994 | 0.2669 | |
| Zip-in | 0.1245 | 0.1261 | 0.1287 | 0.1838 | 0.1989 | 0.2669 | |
| Metalized satin | | | | 0.1069 | 0.1228 | 0.1861 | |

and the area of the fabric in square centimeters. All statements as to the significance of differences among fabrics and combinations of fabrics have been substantiated by analyses of variance or by least significant differences calculated from them.

## Differences between Measured and Added Values

The thermal insulation values obtained by direct measurement of the combinations of fabrics are given in Table II and totals for the thermal insulation values for the indiivdual fabrics involved in Table III. A highly significant difference has been found between these two sets of data.

While the measured values are consistently larger than the added values, wide variations in the magnitude of such differences are observed, these differences ranging from 0.0060 to 0.2591°C sec m²/cal. The significant differences in thermal insulation between the added and measured values for some of the combinations of fabrics may be due to the fact that in these combinations sufficient air was held between the fabrics to cause a measurable increase in thermal insulation. Those combinations in which poor contact may be made between fabrics due to rough or irregular surfaces were found to have the largest differences between the measured and added values. The reverse was found for combinations made up of fabrics with smooth surfaces. From these observations, it may be concluded that accurate estimates of the insulating capacity of multiple layers of fabrics will be obtained by adding values for the individual fabrics involved only if they have smooth surfaces. If the individual fabrics have rough or irregular surfaces, the fabric combination must be measured directly.

The thickness of fabrics also is closely associated with thermal insulation and consequently differences between the measured and added thickness values for combinations may account for the observed differences in insulation. The sums of the thickness values for the individual fabrics, as shown in Table IV, were in some cases larger and other cases smaller than the measured values for the fabric combinations (Table V). Although few significant differences could be demonstrated, differences between thickness values obtained by the two methods often were numerically larger for those combinations that had

**TABLE V. Mean Added Thickness Values for Multiple Layers of Fabrics**

| Lining or Lining Combination | Coatings | | | | | | |
|---|---|---|---|---|---|---|---|
| | 100% Worsted | 40/60% Worsted | 30/70% Worsted | Light Woolen | Medium Woolen | Heavy Woolen | Dynel Mixture |
| | | | | (in.) | | | |
| 75% alpaca | 0.2262 | 0.2226 | 0.2270 | 0.2731 | | | 0.2317 |
| 50% alpaca | 0.2074 | 0.2038 | 0.2080 | 0.2543 | | | 0.2129 |
| Rayon, quilted | | | | 0.4097 | 0.4305 | 0.4914 | |
| Wool, quilted | | | | 0.2900 | 0.3108 | 0.3717 | |
| Metalized wool, quilted | | | | 0.2449 | 0.2657 | 0.3266 | |
| Interlining | | | | 0.1779 | 0.1987 | 0.2596 | |
| Zip-in | 0.1408 | 0.1373 | 0.1416 | 0.1877 | 0.2085 | 0.2694 | |
| Metalized satin | | | | 0.1037 | 0.1245 | 0.1854 | |

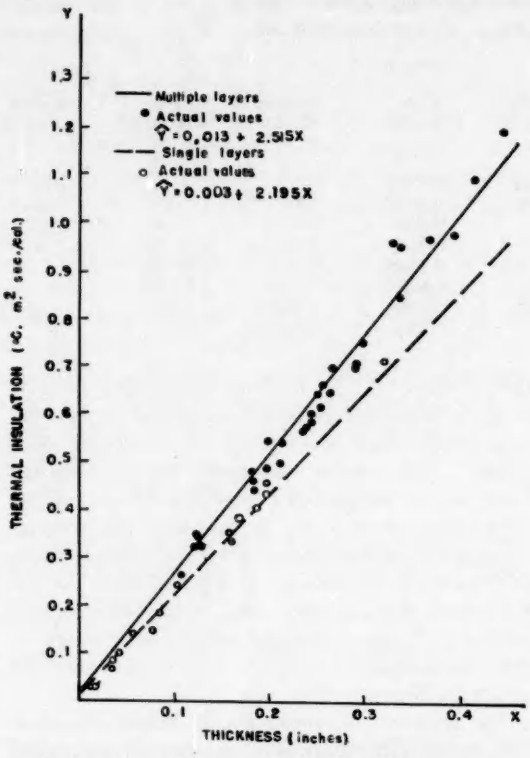


**Fig. 1.** The relationship of thermal insulating capacity to the thickness of single and multiple layers of fabrics, showing the linear regression lines.

been found most often to have significantly larger measured than added values for thermal insulation. The coefficient of correlation between these two variables, $r$, was 0.68, which is highly significant. The square of $r$, the coefficient of determination, shows that proportion of the variance in the values for the dependent variable, thermal insulation, which can be explained by, or estimated from, the concomitant variation in the values for the independent variable, thickness. Therefore, since the square of $r$ equals 0.46, apparently 46% of the differences in thermal insulation are related to differences in thickness.

The fact that considerably greater changes were observed for thermal insulation than for thickness indicates that enough air may be enclosed between the layers of fabrics to cause a significant increase in thermal insulation without at the same time causing a measurable change in thickness.

## Relationship between Thermal Insulation and Thickness

Thermal insulation data for the single and multiple layers of fabric were plotted against (1) values for thickness and (2) values for air per unit area of fabric in order to point out that fabric characteristic from which thermal insulation may be estimated most accurately. The relationships found for the single fabrics have been compared with similar relationships for the multiple layers of materials in order to determine any existing similarity.

The relation of thermal insulation to the thickness of the single and multiple layers of fabrics, respectively, as well as the linear regression lines and equations illustrating this relationship are shown in Figure 1. It demonstrates the linear relationship which has been found for both the single and multiple layers of fabrics used in this study. Many investigators have observed previously that there is a linear relationship between thermal insulation and thickness.

Although Speakman and Chamberlain [6] have reported an increase in thermal insulation with an increase in thickness, Morris [4] points out that an

inspection of their results shows that this relationship holds only for thicknesses below about 0.055 in. Also Baxter [1] found thermal insulation values to have a linear relationship to thickness up to 0.395 in., but where materials exceeded this thickness he found that the slope of the insulation-thickness curve fell off rapidly and appeared to become horizontally asymptotic. From Figure 1 it may be seen that no apparent tendency for these insulation-thickness curves to become vertically or horizontally asymptotic is shown, although most of the single fabrics and all of the combinations of fabrics used in this investigation exceed 0.055 in. in thickness and two fabric combinations exceeded 0.394 in. While the two combinations that exceeded 0.394 in. in thickness when measured gave higher insulation values than would be estimated from the linear regression equation, nevertheless they fall within one standard deviation of the estimated value. Therefore, it may be concluded that a linear relationship exists between thermal insulation and thickness for both the single and multiple layers of these fabrics, although these relations do not hold, necessarily, beyond the limits of the thickness measurements.

Accurate estimates for the thermal insulating capacity of multiple layers of fabrics may not be made from the equation based on single fabric measurements. To illustrate this statement, the thermal insulation for a combination of fabrics 0.3 in. thick, which is within the limits of both equations, could be used. The estimated insulation would amount to 0.6715°C sec m²/cal from the equation based on the single fabric measurements

$$\hat{Y} = 0.003 + 2.195X$$

where $X$ is thickness in 0.001 in. at a pressure of 0.02 lb/in.² On the other hand, from the multiple layer equation,

$$\hat{Y} = 0.013 + 2.515X$$

the estimated insulation would amount to 0.7675°C sec m²/cal. Since the standard error of estimate for the single fabric equation is 0.0105, approximately 68% of all fabrics 0.3 in. thick might be expected to have insulation values varying from 0.6609 to 0.6819°C sec m²/cal. The chance that a fabric of this thickness would have an insulation value of 0.7675, as obtained from the fabric combination equation, is practically zero since it is more than three standard deviations greater than the estimated mean.

The slope of the linear regression line calculated for the single fabrics is less than that for layers of fabrics and the intercept of the ordinate is higher for the latter regression line; consequently, the differences between the estimated values become greater as thickness values increase.

Since the regression coefficient for the multiple layers of fabrics is larger, 2.5153, than that for the single fabrics, 2.1948, a given unit increase in the thickness of the multiple layers is associated with a greater increase in insulation than would be the case for the single layers. In explanation, it might be claimed that the increasing thickness of multiple layers of fabrics is associated with larger concomitant increases in the total amount of air held within the structure than would be the case for single fabrics.

The insulation-thickness coefficients of correlation for both the single and multiple layers of fabrics used in this study are very high, 0.998 and 0.96, respectively, and in good agreement with those reported by Winston and Baxter [8].

The standard error for the single fabrics is 0.0105, although, as stated previously, the equation may be considered valid for estimating insulation only for single fabrics within the thickness range of 0.0171 to 0.3231. This standard error is lower than that found for volume of air per unit area (0.0141). Therefore, thickness will give the most accurate estimates of thermal insulating capacity for single fabrics under the conditions specified in this investigation. Thickness, however, does not give equally accurate estimates of insulation for multiple layers of fabrics. The standard error of estimate for the multiple layers of fabrics, when thickness was the independent variable, was 0.0728, while it was only 0.0358 when air per unit area was the independent variable. Consequently, for estimating the thermal insulation of multiple layers of fabrics, the equation based on air per unit area and insulation will give greater accuracy than that based on thickness and insulation measurements.

### Relationships between Thermal Insulation and Air-Space Properties

The volume of air per unit area, porosity, and density all are measurements of the air-space properties of single and multiple layers of fabrics. Since the air space in a fabric is one of the main factors which determine its insulating capacity, a high correlation between these factors and thermal insulation

could be expected. The volume of air per unit area was found to be more closely associated with variations in thermal insulation than with porosity or density.

The linear relationships found between the volume of air per unit area of a fabric and thermal insulation are illustrated in Figure 2. The slope of the regression line for the multiple layers of fabrics is greater and the ordinate intercept higher than for the single fabrics. Consequently, as with the equations calculated from thickness and thermal insulation measurements, if the thermal insulating capacity of combinations of fabrics were to be estimated from the equation for the single fabrics, such a value would be low. Thus, it may be concluded that the equation calculated for the single fabrics will not give accurate estimates of thermal insulation for combinations of fabrics.

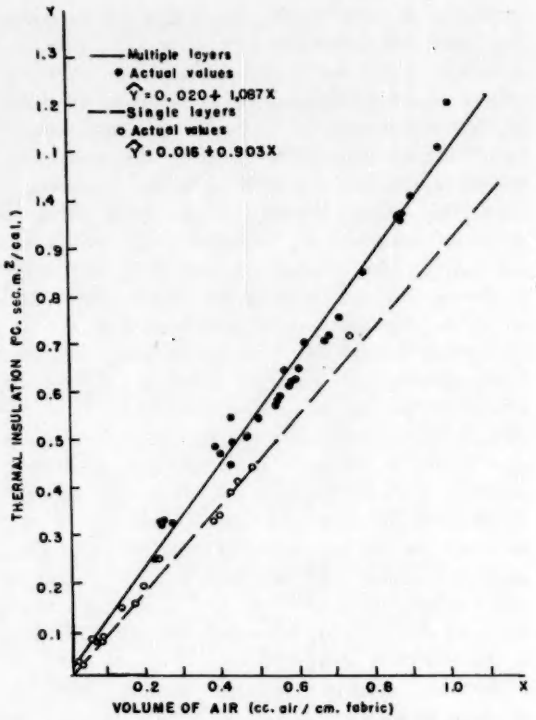


**Fig. 2.** The relationship of thermal insulating capacity to the volume of air of single and multiple layers of fabrics, showing the linear regression lines.

## Summary

Thermal insulation, thickness, and volume of air per unit area of fabric have been determined for single and multiple layers of fabrics. Various coatings, linings, and interlinings, and combinations of these materials commonly found in ready-to-wear winter outer garments were included in this investigation. The data obtained and their interpretation permit the following summary statements:

1. Accurate estimates of the insulation of multiple layers of fabrics will be obtained by adding values for the individual fabrics involved only if the fabrics have smooth surfaces. If the individual fabrics have rough or irregular surfaces, the fabric combination must be measured directly. The differences observed between added and measured values for thermal insulation can be explained in part by concomitant changes in thickness. The fact that considerably greater changes are observed for thermal insulation than for thickness indicates that enough air may be enclosed between the layers of fabrics to cause a significant increase in thermal insulation without, at the same time, causing a measurable change in thickness.

2. A close linear relationship exists between thermal insulation and thickness and between thermal insulation and volume of air per unit area for both single and multiple layers of fabrics. While thermal insulating properties of single fabrics can be estimated most accurately from thickness measurements, the volume of air per unit area provides the best basis for estimating the thermal insulation of multiple layers of fabrics.

3. Thickness and volume of air are highly correlated with thermal insulation, indicating that a large proportion of the differences in thermal insulating capacity may be accounted for by these properties.

4. Linear regression lines, representing the relationship between thermal insulation and other properties, for the single fabrics give lower estimated values than do those for the multiple layers of fabrics. Therefore, accurate estimates of thermal insulation for multiple layers of fabrics may be made only from equations based on measurements of such combinations.

## Acknowledgments

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# Effects of Nuclear Radiation on the Strength of Yarns

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RECENT published reports have indicated an improvement in the physical properties of various plastics by nuclear irradiation, and these results suggested the possibility of attaining improvements by similar irradiation of textile fibers. Since strength of a fiber is generally of primary importance, this was the first property investigated. Due to the very nature of the type of irradiation contemplated, it was decided to restrict the initial work to yarn rather than fiber per se. The yarns selected for treatment were 60/2 mercerized cotton, 50/1 spun viscose, 70/34 nylon, and 200/80 Type 81 Orlon.[1] Samples from each lot of yarn were prepared in triplicate: one for "control," one to be exposed to gamma irradiations in the order of about 10,000,000 r (Series A), and the other (Series B) to be given at least 24 hr of neutron irradiation.

In order to obtain an approximate idea of the dose of radiation required, it was necessary first to speculate as to the mechanism of physical changes which could be expected to strengthen the fiber. It was assumed that two competing physical changes take place in an irradiated fiber: one is crosslinkage of the polymer chains, tending to strengthen the fiber, and the other chemical degradation, tending to break the chains and to some extent to destroy the crosslinkage previously formed by the irradiation, hence weakening the fiber. If the first predominates, the initial effect of irradiation should be to strengthen the fiber due to the gain from crosslinkages outweighing the loss of strength by chain breaking. However, the increase in strength with degree of dose would not be expected to increase indefinitely. It is felt that as the dose increases the time must come when the breakage of crosslinkages already formed by the radiation bombardment plus the chain breakages will balance the good effect of the formation of new crosslinks. At this dose, the fiber will have its maximum strength.

To form the crosslinkage, the mechanism envisioned was of some of the nuclear radiation (Klein-Nishina electrons in the case of gamma radiation and recoil protons in the case of neutron irradiation) dislodging the atoms from the chemical chains of the fibers. It was further assumed that some of these

[1] Du Pont acrylic fiber.

**TABLE I. Single-End Strength of Various Irradiated Yarns**

| Yarn | Control Yarns | | Irradiated Yarns | | | |
|---|---|---|---|---|---|---|
| | | | Gamma (Series A) | | Neutron (Series B) | |
| | Dry | Wet | Dry | Wet | Dry | Wet |
| 60/2 Combed American Mercerized Cotton | 467.0 | 520.0 | 292.0 | 210.0 | 10.0 | 0 |
| 50/1 Spun Viscose 1.0 × 1½ in. Bright | 177.2 | 108.0 | 86.5 | 38.8 | Too brittle to test | |
| 70/34/0 Nylon, Type 100 | 397.5 | 347.5 | 179.0 | 158.0 | 188.0 | 170.0 |
| 200/80/0 Orlon, Type 81 | 642.0 | 672.0 | 653.8 | 646.0 | 492.0 | 474.0 |

**TABLE II. Tenacity (G/den) of Various Irradiated Yarns**

| Yarn | Control Yarns | | Irradiated Yarns | | | |
|---|---|---|---|---|---|---|
| | | | Gamma (Series A) | | Neutron (Series B) | |
| | Dry | Wet | Dry | Wet | Dry | Wet |
| 60/2 Combed American Cotton | 2.64 | 2.94 | 1.65 | 1.19 | 0.05 | 0 |
| 50/1 Spun Viscoxe 1.0 × 1½ in. Bright | 1.67 | 1.02 | 0.81 | 0.37 | 0 | 0 |
| 70/34/0 Nylon, Type 100 | 5.70 | 4.95 | 2.56 | 2.26 | 2.69 | 2.43 |
| 200/80/0 Orlon, Type 81 | 3.21 | 3.36 | 3.27 | 3.24 | 2.46 | 2.37 |

**TABLE III. Approximate Per Cent Loss in Single-End Tenacity of Various Irradiated Yarns (Based on Control Yarns)**

| Yarn | Irradiated Yarns | | | |
|---|---|---|---|---|
| | Gamma (Series A) | | Neutron (Series B) | |
| | Dry | Wet | Dry | Wet |
| 60/2 Combed American Mercerized Cotton | 35 | 60 | 98 | 100 |
| 50/1 Spun Viscose, 1.0 × 1½ in. Bright | 51 | 64 | 100 | 100 |
| 70/34/0 Nylon, Type 100 | 55 | 55 | 53 | 51 |
| 200/80/0 Orlon, Type 81 | 0 | 0 | 24 | 30 |

empty spaces would then be filled by atoms from adjoining chains, thus forming a crosslinkage.

Assuming the foregoing theory to be generally correct, two main questions must be answered by experiment for each fiber under consideration: (1) Does the fiber initially gain strength at small doses or does it lose strength from the start? (2) If it initially gains in strength, what dose gives it the maximum strength?

The first step was to calculate the order of magnitude of dose of gamma rays which would be expected to give the greatest increase in strength, if the "most favorable dose" does exist. Although three different polymers were irradiated, the calculation of optimum dose was made only once, for cellulose. Then all three polymers were exposed to approximately this much radiation, although it was realized that individual differences may be expected for each particular polymer. It was assumed that one crosslink per 20 cellulose units, in the case of cotton, would give maximum strength. This corresponds to 0.0003 m of crosslinkages per gram of cellulose. Further, it was estimated from Gaydon's *Dissociation Energies and Spectra of Diatomic Molecules* that approximately 100,000 cal/m would be required to break a linear carbon-carbon bond and form a cross-carbon-carbon bond. This corresponds to 30 cal or 200,000,000 ergs/g. Assuming for this work that the density of cellulose from gamma-ray flux would be approximately 1000 ergs/r, then, based on the above, the degree of crosslinkage assumed necessary for maximum strength would require a dose of about 200,000 r if the process of formation of crosslinks were 100% efficient. Yet it was difficult to imagine a mechanism whereby the efficiency of this process could exceed 2%; therefore, it was concluded that the optimum dose might be approximately 10,000,000 r. Thus it was decided to confine the initial investigation on the three polymers to this dose. It should be pointed out here that as yet there is no evidence that the phenomenon occurs at all, thereby making it impossible to estimate directly the upper limit of the dose required; however, regardless of the bond-breaking efficiency of gamma rays and/or neutron bombardment, it must be realized that there will be extensive degradation of cellulose at doses above 20,000,000 r whether crossbonding occurs or not.

## Procedure

The Brookhaven National Laboratory kindly consented to irradiate the yarns under investigation. Duplicates of each were sent to them. It is understood from them that Series A was irradiated in a gamma field produced by a cobalt 60 source in which the predominant gamma-ray energy was estimated at 1.3 Mev. The yarns, irradiated for 42 h, received a total of 8,400,000 r. Simultaneously, they irradiated Series B for 26 h in the water-cooled section of the pile at Brookhaven. These it is understood were given a dose of $2.3 \times 10^{17}$ neutrons per square centimeter. Of these neutrons, 5 out of every 6 had approximately thermal energy—the sixth was a fast neutron (1 Mev or faster).

Due to the limited amount of space allotted to us in the pile, the size of the samples irradiated restricted the evaluation to single-end testing, "dry" (at standard atmosphere—65% R.H. at 70°F) and "wet" (in accordance with ASTM Standard D258-52T).

The effect of gamma and neutron irradiation on the strength of the various fibers is shown in Tables I, II, and III. In addition there is included (Figures 1–4) representative stress-strain curves of the cotton, viscose, nylon, and Orlon yarn, as obtained on a Scott IP2 Single End Serigraph machine.

## Discussion

It is felt at this time that the discussion should be as general as possible due to the uncertainties that can be expected with initial experimental work of this nature. Therefore, both the discussion and conclusions will be limited to the obvious, as indicated by the results.

*Figure 1: 60/2 Combed American Mercerized Cotton*

The gamma irradiation lowered the ultimate breaking strength of the cotton yarn, "dry" and "wet"; however, although the wet strength of "control" cotton yarn was initially about 10% greater than its "dry" strength, the wet strength of the gamma-irradiated cotton was about 55% less than the dry

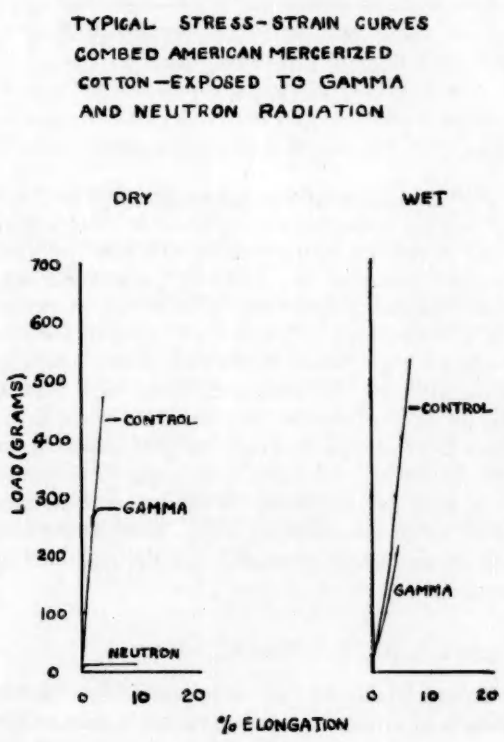


Fig. 1.

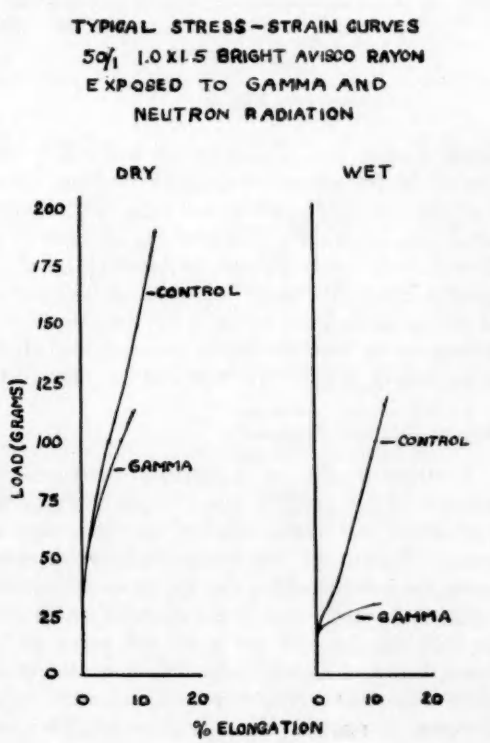


Fig. 2.

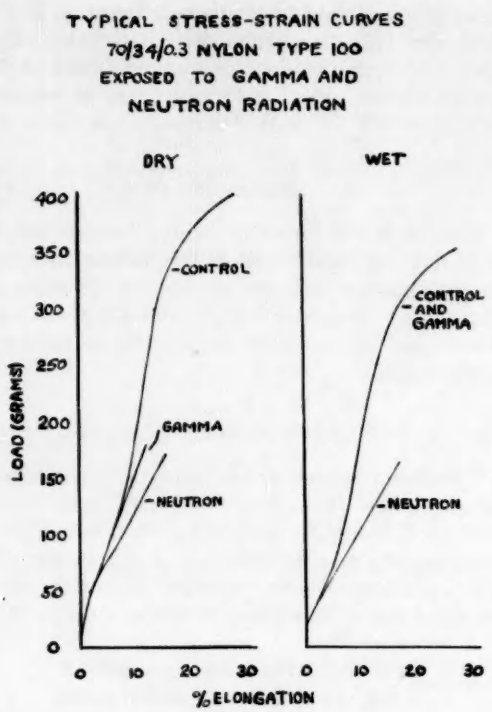


Fig. 3.

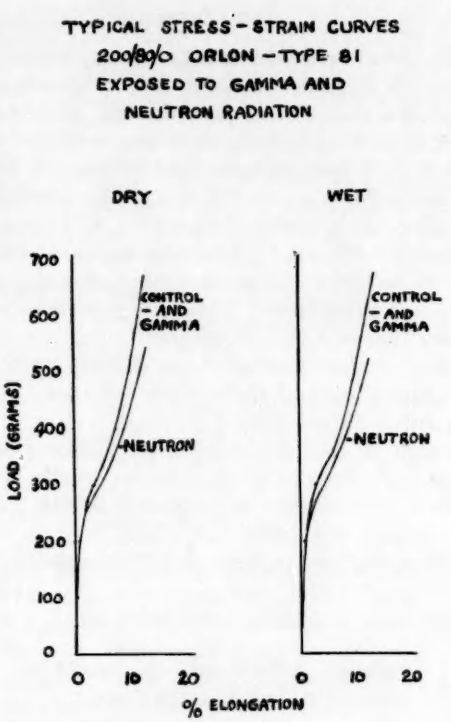


Fig. 4.

strength of the control cotton and had nearly twice the loss in strength—control versus irradiated yarn—that the dry gamma-irradiated yarn did. Neutron irradiation practically destroyed the strength of the fiber, dry and wet. Up to its breaking point, the gamma irradiation caused no observable differences in stress-strain characteristics of the "dry" yarn. However, the "wet" irradiated yarn indicated greater susceptibility to extension than did its control yarn.

*Figure II: 50/1 Viscose*

Neutron irradiation completely destroyed the strength of the yarn. Gamma irradiation generally reproduced the trends obtained on the mercerized cotton. Within the limits imposed by experimental error, the indications are that the gamma irradiation reduced the "dry" and "wet" strength by 50–60%. In both the dry and wet state, the yarns, at low stress, indicated no observable differences in extensibility with respect to their respective control yarns; however, a marked increase in extensibility was noted for both at higher stresses.

*Figure III: 70/34/0 Nylon, Type 100*

Both gamma and neutron irradiation reduced the dry and wet strength about equally. In other words, a loss in strength of between 50–60% was indicated for the Nylon yarn, dry and wet, gamma and neutron irradiated, respectively. No change in stress-strain characteristics was detected for the gamma-irradiated yarn, tested in the wet state; however, in the dry state, the gamma-irradiated yarn became slightly more susceptible to stretch as the stress increased. The neutron-irradiated yarn exhibited, in both the dry and wet tested state, a sharp divergence from what is considered the normal stress-strain curves of Nylon—as noted above, both gamma and neutron irradiation produced about the same loss in strength.

*Figure IV: 200/80/0 Type 81 Orlon*

Gamma irradiation had no apparent effect on the strength of Orlon. Neutron irradiation reduced the strength, but less than it did on the other fibers.

Neutron irradiation had no observable effect on the extensibility properties of the Orlon up to a stress point of about 50% of the ultimate breaking strength. After this point, which was at just about the same level for "dry" and "wet," the yarn exhibited a less orientated condition than the control yarns and the gamma-irradiated yarns.

It will be noted from the above that Orlon and Nylon both exhibited less loss in strength than did the two forms of cellulose. This may be due to the fact that when a cellulose chain is broken by radiation it remains in this condition because carbon has just one valence and therefore so little flexibility in the formation of other polymers. On the other hand, nitrogen can have more than one valence and is well known to form compounds such as the ammoniate and ethylene diamine complexes with metals in which its secondary valence forces are exerted. It may be that when a nitrogen atom is freed from its linkages in the polymer, it may form more readily new linkages of a similar type than would a carbon atom. The nitrogen atom may also be expected to form more readily crosslinkages because of its long-range valence forces, which carbon does not possess. Thus, to speculate, the polymers that contain nitrogen may show an initial increase in strength with radiation while possibly the carbon polymers may be weakened since they contain no atom capable of exerting long-range valence forces.

## Conclusions and Summary

Within the uncertainties of this investigation, the indications are that:

1. The gamma irradiation seriously weakened the cellulosic fibers and Nylon but had no visible effect on the strength of the Type 81 Orlon.

2. Neutron irradiation weakened all of the fibers tested. However, since no common basis is known to us which would allow the gamma irradiation and neutron irradiation to be put on a comparable basis, it is felt that no comparisons should be made between relative losses in yarn strength—gamma produced versus neutron produced.

3. For the same amounts of neutron irradiation, the cellulosic fibers were weakened to such a degree that it was impractical to test them. The strength of Orlon was reduced by about 25–30%, as against a 50–55% loss in strength of Nylon.

4. Where it was possible to test a neutron-irradiated yarn, the stress-strain characteristics were visibly changed, indicating always a fiber more susceptible to stretch for a given stress. The greatest change noted was for Nylon. Gamma irradiation was less consistent in this respect, with no observable effect on dry cotton, wet and dry Orlon, and wet Nylon, and only a small change otherwise.

To summarize, it can be concluded that all of the yarns investigated were injured at the level of radiation used in this experiment. This does not prove that it is impossible to improve the strength properties of yarns by irradiation, but suggests that if such an improvement is possible, it will be found at lower doses than those used here.

### Glossary

| | |
|---|---|
| *Recoil Proton:* | A hydrogen nucleus knocked out of a molecule by a neutron. |
| *Klein-Nishina Electron:* | An electron knocked out of an atom by a gamma ray. |
| *"Fast" Neutron:* | A neutron that as yet has not come to thermal equilibrium with its surroundings. When a neutron is first formed in the fission process, it is moving at a rate at least in excess of 10,000,000 mph. Then, by successive collisions with atoms of the material through which the neutron passes, it loses speed and ultimately arrives at a velocity whereby there is equal chance that the next collision will slow it down or speed it up. At this velocity it is at thermal equilibrium with the material. |
| *Thermal Neutron:* | A neutron that has reached thermal equilibrium. |

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# Heterogeneous Degradation of Cellulose

## IV. Mild Hydrolytic Degradation of Cotton and Wood Pulp[1]

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**Abstract**

The presence of a wetting agent (Igepon) accelerated only the initial degradation of a raw cotton exposed to 0.1 *N* hydrochloric acid at 20°C in the absence of light for periods of up to 350 days. During this time the dry strength decreased by almost one-half. The dry strength decrease, being slightly greater than the wet strength decrease, resulted in a small relative wet strength increase, from 93% to 110%. Purified cotton linters were degraded more slowly than raw cotton, and an alkaline refined sprucewood pulp more slowly still, even though the wetting agent was present in the latter case.

In 1948 Kleinert and Moessmer [3] published a preliminary note on an attempt to eliminate any effect of diffusion on the rate at which cellulose was degraded by dilute aqueous acids. Raw cotton was degraded so slowly that diffusion was not likely to be a rate-controlling factor, 0.1 *N* aqueous hydrochloric acid being used at 20°C in the dark for periods of up to 350 days. Nevertheless, the inclusion of a wetting agent, Igepon, accelerated the initial rate of degradation. In this paper these experiments are recorded in greater detail, together with additional results on purified cotton linters and on a refined wood pulp.

The data summarized in Figure 1 clearly showed that the use of the wetting agent Igepon facilitated the degradation of chemically untreated raw cotton until the "limit D.P." was approached in about 100 days; thereafter the wetting agent had little or no effect (curves I*a* and I*b*). A mass of evidence, described in standard textbooks [6, 9] suggests that the rapid initial decrease in degree of polymerization during heterogeneous hydrolysis represents the cleavage of glycosidic bonds in the amorphous portion [5, 7] of the cellulose fiber. On this basis, the wetting agent made the amorphous portion more accessible to the acid, presumably by dispersing the naturally occurring water-repellant fats and waxes. A comparison between curves I*a* and II brought out the fact that kier-boiled and bleached cotton linters were degraded more slowly than raw cotton. This observation could not be explained by a greater

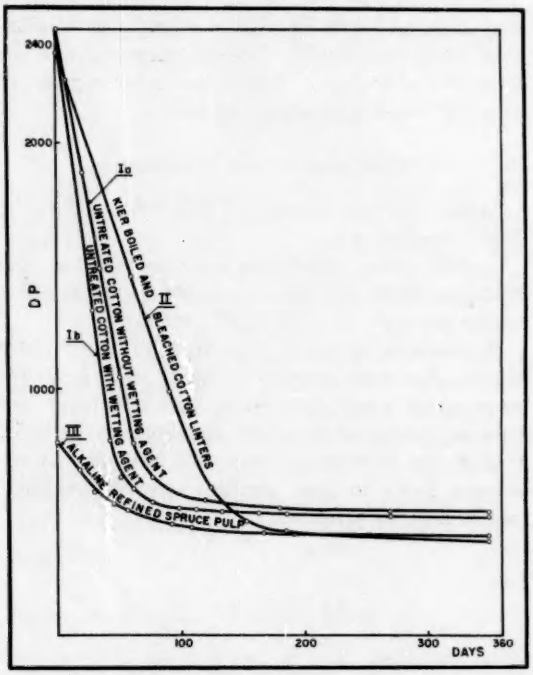


**Fig. 1.** Hydrolytic degradation of cellulose in 0.1 *N* HCl with and without a wetting agent.

[1] These investigations were carried out at the research laboratory of Zellwolle Lenzing Akt. Ges., Lenzing, Austria. The authors wish to thank the Company for permission to publish the work.

[2] Present address, Pulp and Paper Research Institute of Canada, Montreal, Quebec.

**TABLE I. Textile Properties of a Raw Cotton during a Very Slow Degradation by Dilute Acid***

| Hydrolysis (Days) | Breaking Length, km | | Extension (%) | | Relative Wet Strength (%) | Abs. Loop Strength (km) |
|---|---|---|---|---|---|---|
| | Dry | Wet | Dry | Wet | | |
| 0 | 24.7 | 23.0 | 17.3 | 18.9 | 93.1 | 12.7 |
| 29 | 22.6 | 21.8 | 17.1 | 20.1 | 96.5 | 12.6 |
| 43 | 22.4 | 21.4 | 17.1 | 20.5 | 95.6 | — |
| 51 | 22.3 | 21.4 | 17.0 | 20.8 | 95.9 | 12.4 |
| 62 | 22.1 | 21.3 | 16.9 | 21.1 | 96.3 | — |
| 77 | 21.6 | 21.0 | — | — | 97.2 | 12.3 |
| 98 | 20.2 | 19.3 | 17.2 | 21.7 | 95.5 | 11.2 |
| 113 | 18.7 | 17.7 | — | — | 94.7 | 10.6 |
| 134 | 16.6 | 16.6 | — | — | 100.0 | 9.5 |
| 163 | 14.8 | 15.6 | 17.0 | 22.5 | 105.5 | — |
| 186 | 13.9 | 15.2 | 17.1 | 22.7 | 109.4 | 7.5 |
| 270 | 13.6 | 14.9 | — | — | 109.6 | — |
| 350 | 13.5 | 14.8 | 17.0 | 24.0 | 109.6 | 7.1 |

* Degraded in dark by 0.1 *N* hydrochloric acid at 20° C and containing 2 g of Igepon per liter.

amount of recrystallization undergone by the purified sample during hydrolysis because the "limit D.P." of the linters was lower, not higher, than that of the cotton. Either the linters were intrinsically less accessible or they had become so during the process of purification. The relatively slow initial rate of degradation of the alkali-refined wood pulp, even though a wetting agent was present, confirmed the findings of Samuelson et al. [8]. In all four cases the "limit D.P." representing the average chain length of the cellulose crystallites was in the range expected for very slow hydrolyses attended by much recrystallization of the fragmented macromolecules; hydrolyses rapid enough to give little opportunity for recrystallization usually yielded a "limit D.P." of approximately half the above values [2, 6, 9] and even lower [7].

With kier-boiled and bleached cotton and also with alkaline refined wood pulp (alpha-cellulose, 94.6%; cuprammonium viscosity in 1% pulp solution, 24.5, centipoises) no considerable decrease of acid was found, whereas in the series using raw cotton a small acid consumption appeared in the 100-day run, corresponding to 0.0895 g HCl per 100 g cotton. It is to be noted that the amounts of cellulose becoming soluble during mild hydrolytic degradation are relatively small [2]. In the cotton series the weight loss within a year was less than 2% of the total fiber weight.

Although others [4, 7] followed the changes in relative wet strength and in elongation when cellulose fibers were in process of degradation by acid, it seemed worthwhile to extend the measurements to a case in which the opportunity for recrystallization was unusually great. The raw cotton (D.P. 2460; fiber length 28–30 mm) was examined in this way undergoing the degradation recorded in curve I*b* of Figure I. As the hydrolysis progressed, the dry strength decreased more rapidly than the wet strength until the relative wet strength became even greater than unity. At the same time the elongation of the wet fiber increased markedly while the value for the dry fiber remained unchanged. These findings suggested that the loss of tenacity caused by degradation was offset to a slight extent in the wet fiber by a greater ability to orient under tension. (Table I)

From the experiments no conclusive evidence is apparent of faster splitting links in the cellulose chains.

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# The Role of the Hydrogen Bond in the Rheological Behavior of Cellulose Sheets

**Alfred H. Nissan**

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## 1. Introduction

The hydrogen bond is a weak linkage between molecules and "it has more in common with the forces present in 'van der Waals molecules' than with any other" [3]. Thus, properties which are themselves evidences of secondary forces are peculiarly suited to measure them—e.g., the second virial coefficient in the equation of state, the vibrations in the infrared and dipole polarization effects. Thermochemical methods, so well suited to the very much stronger covalent bonds, for instance, are difficult to apply with accuracy since the weakness of the hydrogen bond demands a smaller scale and unit of measurement. Mechanical properties, due to the large value of $J$, the mechanical equivalent of heat, may become particularly suitable measures where these bonds are plentiful. Grunberg and Nissan [5], for instance, attempted to evaluate these bonds from viscosity and surface-tension data of hydrogen-bonded liquids.

The two species of material designated as "paper" and "board" are solids which are overwhelmingly controlled by hydrogen bonds. In these, the fibers of cellulose are disintegrated to individuals, beaten to cause them to fibrillate, and then filtered off in sheets and dried. A cardinal factor in these processes, however, is that the liquid used for disintegration, beating, filtering off, and, finally, which has to be removed by drying, must be water if the sheet produced is to possess useful mechanical strength. The choice of water is not simply for economical reasons or for convenience; if the processes are carried out in benzene, the sheet reveals no more strength than can be accounted for by the entanglement of fibers, frictional forces, and a residuum of bonds between fibers, probably due to the traces of water in fiber and liquid. Conversely, unless the sheet is specifically made resistant its mechanical properties are profoundly affected by its moisure content until at saturation practically all strength disappears.

It is apparent that these materials afford specially favorable opportunities for the study of the peculiarities of the hydrogen bond by mechanical means, or, at least, of the type of hydrogen bonds which exist between cellulose molecules.

## 2. General Mechanical Properties of Cellulosic Sheets and their Interpretation

It will be helpful in crystallizing ideas if the main features of the mechanical properties which are common to all types of these cellulosic sheets are outlined.

The first point to note is that in their behavior these sheets do *not* resemble the fibers of which they are made. Thus a sheet of paper made of cotton fiber will yield a tensile stress-strain curve bent towards the strain axis, while cotton yields a very much less curved line bent towards the stress axis. Or, again, the effect of an increase in moisture content on cotton is to increase its strength; on a sheet of paper made from cotton fibers the effect is to weaken it. The system of bonds stressed in single fibers and in sheets under tension are different; in the fiber the main covalent bond takes part in the straining operation to a far greater extent than happens in a sheet.

The most important positive characteristic of the mechanical properties of these sheets is that their stress-strain curves always have pronounced curvature toward the strain axis.

Only second in importance to the curvature of the line is the fact that such curves are time dependent: At constant stress the sheet creeps; at constant strain it relaxes. It follows, therefore, that the stress-strain curve will be affected by the rate of straining.

Finally, the profound effect of water on the stress-strain curve is a general and very important characteristic.

Recently, Nissan [11] reviewed these properties and the theories for their interpretation and put

forward a theory based on the hydrogen bond. Here only the basic elements of the theory will be given, and a discussion will be made from the viewpoint of elucidating the characteristics of the hydrogen bond from the mechanical properties of paper sheets. The significance of the theory from the point of view of paper properties should be read in *Tappi*.

The theory states that in straining paper only the hydrogen bonds of amorphous regions of the cellulose matrix are strained. As the bonds are assumed to be uniformly distributed, the macroscopic strain is equated to the bond strain. Since the differential coefficient of energy potential of the bond with respect to bond length is not linear, the stress-strain curve of cellulosic sheets will not be linear. The bonds are weak and break readily, yielding creep and relaxation. Finally, it is postulated that a broken bond will reform when it next meets an appropriate portion of another broken bond; thus internal rupture is in part selfhealing. The influence of water is due to substituting a bond between water and cellulose, which contributes little to the stress, for one between cellulose and cellulose.

## 3. The Stress-Strain Curve of Cellulosic Sheets as Predicted from the Hydrogen Bond Theory

### 3.1 *Basic Equations*

Let a sheet be strained by $(\delta\sigma)$ and let the stress immediately observed be $f$ d/cm². The energy imparted into the sheet is $(f\delta\sigma)$ ergs/cm³. According to the present theory this energy goes into stretching hydrogen bonds so that their potentials are raised from $(-U_o)$ at equilibrium to $(-U_o + \delta U)$ ergs/cm³. (Note that $U_o$ is energy per unit volume of strained material, *not* per mole of hydrogen bonds.) Thus

$$f = \delta U/\delta\sigma \tag{1}$$

or, working with infinitesimally small strains,

$$f = dU/d\sigma \tag{2}$$

It is therefore necessary to find an expression for $U$ in terms of $\sigma$. It is assumed that these bonds are uniformly distributed and that for a macroscopic strain $\sigma$ each bond will be strained by $\sigma$ too. Thus, any of the functions connecting bond potential with separation distance can be transformed into a $U(\sigma)$ function. The Morse potential [10][1] modified from its usual appearance is found to be a convenient and useful function for this purpose; i.e.,

$$U = U_o[e^{-2a\sigma} - 2e^{-a\sigma}] \tag{3}$$

It is interesting to note that the constant $a$ is connected with the negative (compressional) strain $\sigma^*$ at which $U = 0$ by

$$a = -\ln 2/\sigma^*$$

By differentiating equation (3) with respect to $\sigma$, the fundamental equation connecting stress and strain is obtained directly.

$$f = 2aU_o[e^{-a\sigma} - e^{-2a\sigma}] \tag{4}$$

It is found advantageous, however, to expand the exponential terms so that a polynomial is obtained as in equation (5):

$$f = 2a^2U_o[\sigma - (3/2)a\sigma^2 + (7/6)a^2\sigma^3 - \cdots] \tag{5}$$

As $(f/\sigma)_{\sigma=0} = 2a^2U_o = E$, Young's modulus in dynes/cm², equation (5) can be put in one of two forms shown as equations (6*a*) and (6*b*), respectively:

$$f = E\sigma - (3/2)aE\sigma^2 + (7/6)a^2E\sigma^3 \tag{6a}$$

$$= E\sigma - (9E^3/8U_o)^{\frac{1}{2}}\sigma^2 + (7/12)(E^2/U_o)\sigma^3 \tag{6b}$$

Up to $\sigma = 0.01$, the fundamental equation simplifies, within experimental error, to

$$f = E\sigma - K\sigma^2 \tag{7}$$

where

$$E = 2a^2U_o$$

and

$$K = 3a^3U_o$$

For strains exceeding 0.01, the third term in equations (6*a* and *b*) becomes of increasing significance. Equations (6*a* and *b*) or even the summation of the series into the original equation (4) cannot be applied when strains exceed $(\ln 2/a)$ since the Morse function gives a maximum for $f$ at this value of the strain. Normally, however, break intervenes before this strain is attained in papers or boards.

### 3.2 *Verification of the Basic Equations*

Equation (4) or its modifications, equations (5), (6), and (7), readily and accurately fit the types of curves obtained for the stress-strain relationships of cellulose sheets. They also provide a basis for the non-Hookean elastic behavior observed with these sheets. Furthermore, they are, at least in prin-

[1] I am indebted to my colleague Dr. L. Peters for the suggestion to use the Morse function.

**TABLE I.**

| | *A* | *B* | *C* | *D* | No. of Points | Average Coefficient of Correlation |
|---|---|---|---|---|---|---|
| Newsprint | | | | | | |
| Machine Direction | 3.59 | −0.912 | −0.0102 | +0.00278 | 333 | 0.88 |
| Cross Direction | 1.41 | −0.390 | −0.00377 | 0.00139 | 220 | 0.83 |
| Kraft | | | | | | |
| Machine Direction | 6.36 | −1.28 | −0.0128 | 0.00291 | 235 | 0.83 |
| Cross Direction | 3.27 | −0.932 | −0.00695 | 0.00158 | 315 | 0.81 |

**TABLE II**

| | Values of $a$ at | | | |
|---|---|---|---|---|
| | −50°C | 0°C | +50°C | Average |
| Newsprint | | | | |
| Machine Direction | 17.4 | 17.0 | 16.3 | 16.9 |
| Cross Direction | 19.4 | 18.4 | 17.6 | 18.5 |
| Average | 18.4 | 17.7 | 17.0 | 17.7 |
| Kraft | | | | |
| Machine Direction | 13.6 | 13.6 | 13.3 | 13.5 |
| Cross Direction | 18.6 | 19.1 | 17.4 | 18.4 |
| Average | 16.1 | 16.3 | 15.3 | 15.9 |
| Average for all papers | 17.2 | 17.0 | 16.1 | *16.8* |

ciple, capable of prediction from nonrheological data, since they are based on the two parameters $a$ and $U_o$, both of which are fundamental to the hydrogen bond function.

3.21 *The parameter* "a." Mark [8] gives equation (8) connecting $k$, the work required to double the equilibrium distance $r_o$ between atoms on the assumption of Hooke's Law, and certain spectroscopic data:

$$k = 2\pi^2\mu r_o^2 C^2 N^2 \tag{8}$$

where

$\mu$ = Reduced mass = $(1 \times 17)/(1 + 17) = 0.94$

$C$ = Velocity of light, $3 \times 10^{10}$ cm/sec

$N$ = Wave number, $cm^{-1}$

$k$ may also be calculated from the elastic constants of the system according to equation (7) on the same hypothetical basis that Hooke's Law will apply up to a unit strain by calculating the work required for such a strain. (It is, of course, the thesis of this paper that the stress-strain curve is not linear for *any* region of strain in paper but that it curves continuously even in the so-called purely elastic region. Nonetheless, the hypothesis of Hooke's Law is usable as it is merely a device for using the slope of the curve at $\sigma = 0$ for the specific purpose of estimating $a$ from spectroscopic and thermodynamic data; it is then discarded forthwith. This work is equal to $\frac{1}{2}E$ or

$$k = \tfrac{1}{2}E = a^2 U_o' \tag{9}$$

where $U_o'$ is the energy per $cm^3$ of amorphous cellulose in a saturated sample of pure wood pulp or $U_o' = (\Delta H/V_m)R$, where $\Delta H$ is the energy of dissociation of 1 M of O—H . . . O bonds in cellulose; $V_m$ is the molar volume of such a bond in the amorphous region, in $cm^3$, and $R$ is the ratio of amorphous to total cellulose present in the sample. (Note that $U_o$ refers to 1 $cm^3$ of *paper;* $U_o'$ to 1 $cm^3$ of pure amorphous cellulose.) Thus

$$a \sim \pi r_o C N (2\mu/U_o')^{\frac{1}{2}} \tag{10}$$

Marrinan and Mann [9] have made a detailed study of the infrared spectroscopy of cellulose and from their work it appears that $r_o$ can be taken as $(2.7 \pm 0.1) \times 10^{-8}$ cms. The value of $N$ for O—H . . . O is not available for cellulose, but by a private communication Davies has very kindly suggested that it is probably not unlike the value for water and formic acid [3] and may be taken as 180 $cm^{-1}$. This value, at best, is probably true to only $\pm 10$ $cm^{-1}$. Davies [3] also reviews the values of $\Delta H$ for hydrogen bonds and notes that for O—H . . . O, the values fall into two categories: Those obtained from the gaseous state fall between 7 and 10 kcals/mole while those obtained from solutions fall between 2.4 and 5 kcal/M. Davies points out that the gas values will be most significant in any theoretical analysis of the bond energy as there are obvious solvent effects on $\Delta H$, which in any case of solutions refers to the heat content difference between the "solvated species." Thus $\Delta H$ will be taken as $8.5 \pm 1.5$ kcals/M $\equiv (3.6 \pm 0.63) \times 10^{11}$ erg/M. It is shown below that $V_m = 151$ $cm^3$/M of *amorphous* cellulose, i.e., $137 \times 1.1$. For wood

pulp the ratio of amorphous to total cellulose is between 0.4 and 0.5 so a value of 0.45 will be taken for $R$. Substituting the values for $r_o$, $N$, $\Delta H$, and $R$, and using the values derived below for $V_m$, $a$ is found to be 19.4 ± 2.1. In estimating the "error" it is assumed

$$(\delta a/a)^2 = (\delta r_o/r_o)^2 + (\delta N/N)^2 + (\delta U_o'/2U_o')^2 \quad (11)$$

This value of $a$ can be compared with that obtained from rheological data provided by Andersson and Berkyto [7]. These workers determined the load-elongation characteristics of a series of newsprint and kraft papers over a range of temperatures from −50°C to +150°C, fitted various equations to the data by a least mean square method, and measured the "goodness of fit" by calculating a correlation coefficient. They found that the "best" equation fitting all the data was (12)

$$S = (A\epsilon + B\epsilon^2) + (C\epsilon + D\epsilon^2)t \quad (12)$$

where

$S$ = Load, kg wt
$\epsilon$ = Elongation, per cent
$t$ = Temperature, °C
$A, B, C, D$ = Constants as detailed in Table I.

Rearranging equation (12) and converting the load into stress in dynes per cm² and the per cent elongation into a strain, equation (13) results:

$$S = f(wd) \times 10^{-6} = (A + Ct)(100\,\sigma) + (B + Dt)(100\,\sigma)^2 \quad (13)$$

where

$w$ = Width of the sample under test, cm
$d$ = Thickness of the sample under test, cm

Thus,

$$f = [(A + Ct)/(wd)] \times 10^8\,\sigma + [(B + Dt)/(wd)] \times 10^{10}\,\sigma^2 \quad (14)$$

or

$$E = \frac{(A + Ct)}{wd} \times 10^8$$

and (15)

$$K = -\frac{(B + Dt)}{wd} \times 10^{10}$$

From equation (7)

$$a = (2/3)(K/E) = -\tfrac{2}{3} \times 10^2 \left(\frac{B + Dt}{A + Ct}\right) \quad (16)$$

In Table II the values of $a$ as calculated by equation (16) applied to the rheological data of Andersson and Berkyto are given.

It will be seen that, although there is some temperature effect, a value of 16.8 ± 3 covers the whole range of values obtained for $a$ for both types of paper and covering a range of temperature of 100°C. The agreement between this value and that obtained from spectroscopy and thermodynamics is not unsatisfactory, i.e., a range of (15.8–19.8) vs. (17.3–21.5). If the data for the machine direction of the kraft paper is ignored—as it appears to be out of step with the rest—the agreement is somewhat better, i.e., a range of (16.3–19.5) vs. (17.3–21.5).

It is perhaps not unreasonable to consider the prediction of the theory to have been fulfilled and to accept the value for $a$, the average from all available data, as being 18 ± 3.

3.22 *The parameter $U_o$.* According to equation (7), $U_o$ can be obtained either from $E$, $K$, or, better than from either since both $E$ and $K$ are empirically determined parameters, from both:

$$U_o = E/2a^2 \quad (17)$$

$$U_o = K/3a^3 \quad (18)$$

$$U_o = \frac{1}{2}\left(\frac{E}{2a^2} + \frac{K}{3a^3}\right) \quad (19)$$

Using Andersson and Berkyto's symbols and units, these three evaluations of $U_o$ become

$$U_o = \left(\frac{A + Ct}{2a^2wd}\right) \times 10^8 \quad (20)$$

$$U_o = -\left(\frac{B + Dt}{3a^3wd}\right) \times 10^{10} \quad (21)$$

$$U_o = \frac{1}{2a^2wd}\left\{\left(\frac{A + Ct}{2}\right) \times 10^8 - \left(\frac{B + Dt}{3a}\right) \times 10^{10}\right\} \quad (22)$$

The authors give the values for $w$ as 1.5 cm for newsprint and 1.0 cm for kraft. No values are reported for $d$ and values usually met with have to be assumed, i.e., 0.005 cm for newsprint and 0.008 cm for kraft. Finally $a$ will be taken as 18 and, since the influence of the temperature is very small indeed, $U_o$ will be calculated by all three equations for 0°C only. This is shown in Table III.

Table II reveals two facts: (1) The agreement between the various ways of calculating $U_o$ for each type of paper is sufficiently close to warrant the

**TABLE III.**

| | $U_o$, ergs/cm³ Calculated by | | |
|---|---|---|---|
| | Equation (20) | Equation (21) | Equation (22) |
| Newsprint | | | |
| Machine Direction | $7.39\times10^7$ | $6.95\times10^7$ | $7.17\times10^7$ |
| Cross Direction | $2.89\times10^7$ | $2.97\times10^7$ | $2.93\times10^7$ |
| Kraft | | | |
| Machine Direction | $12.3\times10^7$ | $9.16\times10^7$ | $10.7\times10^7$ |
| Cross Direction | $6.31\times10^7$ | $6.67\times10^7$ | $6.49\times10^7$ |
| | | Average | $6.8\times10^7$ |

conclusion that the basic equations are probably valid, since $a$ could be derived entirely from spectroscopy, and that $U_o$ is a reasonably well-defined parameter with the dimensions of energy per unit volume. (2) The parameter $U_o$ assumes different values for different papers and for different directions in the same paper.

It was stated that, in principle, both $a$ and $U_o$ are capable of prediction from nonrheological data. As will be seen presently, there are a number of unknown quantities required in predicting $U_o$. An attempt will be made, however, to see what $U_o$ should be on theoretical grounds because (1) such an attempt will define the quantities so required and may encourage some to measure them and (2) the reasons why $U_o$ should differ between and within papers may become explicitly known.

By definition $U_o$ is the dissociation energy in ergs/cm³ of hydrogen bonds in the amorphous region of cellulose. On the other hand, $\Delta H$ is the energy/mole of hydrogen bonds which, as has been shown already, is of the order of $(8.5 \pm 1.5)$ kcals/M or $(3.6 \pm 0.63) \times 10^{11}$ ergs/M. It is necessary to convert $\Delta H$ to $U_o$ by finding out how many moles of hydrogen bonds exist in 1 cm³ of paper.

From the geometry of the cellulose unit, as revealed by X-ray in the crystal (see Howsmon and Sisson [7]) its volume may be taken as $683 \times 10^{-24}$ cm³. As a cellobiose unit in a cellulose chain can form 6 half-hydrogen bonds with its neighbors, the volume associated with a single bond in the crystalline region of cellulose will be $228 \times 10^{-24}$ cm³ approximately. Thus the molar volume of a cellulosic hydrogen bond, in a crystal, is 137 cm³. The energy per cm³, saturated with crystals of cellobiose, will be $2.62 \times 10^9$ erg/cm³. To reduce this figure to the energy per cm³ of paper, it has to be corrected by several factors as follows:

1. The amorphous region is not as compact as the crystalline region and consequently the volume associated with a hydrogen bond will be greater than that calculated from X-ray studies of the crystalline region. Hermans [6] gives data from which the specific volume of the crystalline region appears to be approximately equal to 0.9 times the specific volume of the amorphous region. Let this ratio be $r_v = 0.9$.

2. Paper is not saturated with cellulose. A sheet of paper 0.008 cm $\times$ $10^2$ cm $\times$ $10^2$ cm weighs, on average, 50 g. If it were saturated with solids with specific gravity of 1.5, it would weigh 120 g. Thus only 0.4 of paper is solid—the rest is void. Of the solids only about 0.75 in newsprint and some 0.9 in kraft is cellulose. Thus the volume of cellulose in 1 cm³ is only 0.3 for newsprint and 0.36 in kraft. Let this ratio be $r_c = 0.3$ for newsprint and 0.36 for kraft.

3. Of the total cellulose, only a fraction is amorphous. This fraction differs for different cellulose fibers, but for wood pulp it is of the order of 0.4. Let this ratio be $r_a = 0.4$.

4. Finally, of the hydroxyl groups on the amorphous region, only a fraction is free for forming bonds between cellulose molecules; the rest are occupied with water molecules and other foreign matter. If the regain of the paper is 8% at the humidity prevailing at the time of test and if all this water is assumed attached to the amorphous region, this corresponds to approximately 3 molecules of water per cellobiose unit. Thus only 0.5 of the total number of sites will be free for linking adjoining cellulose chains. Let this ratio be $r_f = 0.5$.

It is seen that to reduce $(\Delta H/V_m)$ to $U_o$—i.e., the figure of $2.62 \times 10^9$ erg/cm³ of crystals of cellulose to the value for 1 cm³ of paper—it has to be multiplied by the four factors $(r_v \cdot r_c \cdot r_a \cdot r_f)$ or by 0.053 for newsprint and 0.065 for kraft, giving $1.4 \times 10^8$ erg/cm³ for newsprint and $1.7 \times 10^8$ erg/cm³ for kraft paper. Thus, if the ratio of the actual value of $U_o$ found to the theoretical value be called $r_t$, it is seen that

$$r_t = U_o/(\Delta H/V_m) \cdot r_v \cdot r_c \cdot r_a \cdot r_f \qquad (23)$$

$U_o/1.4 \times 10^8$ for newsprint

$U_o/1.7 \times 10^8$ for kraft paper

In Table IV the values for $r_t$ are given. Uncertainties in $\Delta H$, $V_m$, $r_v$, $r_c$, $r_a$, and $r_f$ make the values obtained for $r_t$ at present uncertain, probably to $\pm 50\%$ of the values given. Even then, however,

**TABLE IV.**

| | $r_t$ = Ratio of number of bonds actually strained to the maximum theoretically possible. | |
|---|---|---|
| Newsprint | | |
| Machine Direction | 0.51 | 0.36 |
| Cross Direction | 0.21 | |
| Kraft | | |
| Machine Direction | 0.63 | 0.51 |
| Cross Direction | 0.38 | |

the results obtained are deemed to be not unsatisfactory confirmation of the theory as (1) they do not contradict ideas and observations in practical paper making from which $r_t$ is expected not to approach unity but to be less than 1 and (2) in no calculation does $r_t$ come out either impossibly greater than unity or trivially small. (Theoretically, $r_t$ can exceed unity, say, in the machine direction provided the sum total of machine and cross-direction number of bonds does not exceed the theoretical maximum giving an average value for $r_t$ for both directions equal to or less than unity.)

It is seen that in newsprint only a third of the total number of bonds theoretically available are in fact taking part in the straining operation while in kraft about half are doing so. As newsprint is made of the whole wood fiber with its encrustants, this finding does not contradict expectations and, in fact, explains the superior qualities of kraft paper satisfactorily without invoking a new type of bond or mechanism for each type of paper, but relying entirely on the *number* of bonds per unit volume—the bonds being the same for all cellulosic sheets. The unused sites for hydrogen bonds are considered to be (1) occupied by bonds between the amorphous regions and the crystallite edges or other nonyielding components; (2) sterically hindered from taking part in the straining operation by a ring or fence of crystallites or encrustants isolating a portion of the amorphous region; and (3) sites of free hydroxyls due to bonds which ruptured while the experiment was taking place.

Thus, in order to predict $U_o$ from nonrheological data, it is necessary to have accurate simultaneous measurements of $\Delta H$, $V_m$, $r_v$, $r_c$, $r_a$, $r_f$, and $r_t$. All these quantities, with the exception of $r_t$, are measurable by techniques of known accuracy though, as has been indicated, the accuracy of only a few of them is sufficiently high as yet. The measurement of $r_t$, the ratio of the bonds actually joining the amorphous regions to each other to the maximum possible is, as yet, not readily measurable, though optical methods of measuring "bonded areas" by the diffusion of light are being tried.

It will be realized that the craft of the paper maker in beating and subsequent operations on the fibers is greatly concerned with raising $r_c$ and $r_t$ to as near unity as other considerations will allow by making the sheet more dense and more effectively bonded. When $r_c$ and $r_t$ reach unity, any increase in strength is only possible by raising the other ratios nearer to unity. It is apparent, however, that according to the present theory when all these ratios have reached their practical maximums further beating can only *decrease* the mechanical-strength properties of the sheet. The existence of maximums in all beating time vs. tensile strength curves and the uniform increase in strength with the solid fraction or $r_c$ are features which are, of course, well known among paper technologists. The present theory appears to explain the mechanism involved.

Reverting to the theoretical study of the hydrogen bond, what is pertinent here is the suggestion of the present theory that some of these five unused bonds in every six theoretically available were in fact fully joined at the beginning of the tests and broke *during* the experiments. In other words, even if every theoretically possible bond were in fact formed as an interfiber link in these sheets by forming sheets of pure cellulose from solution at infinitely slow rates, $r_t$ would always be found to be less than unity unless the tests were carried out at such a high speed of loading or straining that the number of bonds broken over the period of test was negligible.

### 4. Bond Breaking and Energy Dissipation on Straining Cellulosic Sheets

From the previous section it appears that the most direct way of studying the kinetics involved in this problem is to obtain stress-strain curves for cellulosic sheets of the same type and under identical conditions but at different rates of straining and then to calculate $r_t$ for each test. Since $r_t$ is a direct measure of the number of bonds taking part in the process of straining, its value under different conditions yields basic information from which rates of break and make-up can be derived. Such experiments are not easy to perform as the variability of these sheets is large and as $r_v$, $r_c$, and $r_a$ have all

to be determined together with a better determination of $\Delta H$ and $V_m$ than is available. On the other hand, they are not impossible and, therefore, at least in principle, $r_t$ should be measurable absolutely. At the present time, however, no such data are available quantitatively and accurately.

Thus, to evaluate the dissipation of energy another technique, used by Garner, Nissan, and Wood [4] in analyzing the behavior of viscoelastic liquids into recoverable (elastic) and irrecoverable (viscous) energies will be adopted, without, however, the thermodynamic connotation involved there.

When $\Delta U$ units of energy are imparted to a sheet by straining it, it is postulated that only a portion, $\Delta U_1$, is recoverable; the remainder, $\Delta U_2 = \Delta U - \Delta U_1$, is lost through the breaking up of bonds. (Even if these bonds rejoin afterwards the energy is lost as the sheet will have no tendency to recover its original unstrained dimensions.) The breaking up of these bonds is considered to be due to their thermal agitation and, as a first approximation, therefore, $\Delta U_2$ will be proportional to $(RT)$. For any value of the strain $\sigma$, the constant of proportionality between $\Delta U_2$ and $T$ may be evaluated empirically as

$$\frac{\Delta U_2}{\Delta U} = \frac{\sigma[df/d(RT)]RT}{\sigma f} = (df/dT)(T/f) \qquad (24)$$

For experiments of constant rate of elongation, the rate of straining is very nearly constant up to strains of, say, 0.05. Thus the rate of energy dissipation will be given for any instant in such experiments by $(d\sigma/d\theta)f\left(\frac{(df/dT)T}{f}\right) = (d\sigma/d\theta)(df/dT)T$ where $\theta$ = time.

If the convention of a dashpot of mechanical models is now assumed, the rate of energy dissipation in such a unit will equal $\eta(d\sigma/d\theta)_v^2$ where $\eta$ is the "viscosity of the liquid in the dashpot" at the rate of shear $(d\sigma/d\theta)_v$. Thus, finally,

$$\eta = [(d\sigma/d\theta)(df/dT)T]/(d\sigma/d\theta)_v^2 \qquad (25)$$

Equation (25) should apply to the whole stress-strain curve of cellulosic sheets, but it is easiest to apply it near the upper end of the curve where $(d\sigma/d\theta)$ is very nearly equal to $(d\sigma/d\theta)_v$. Thus, in the upper regions of the curve,

$$\eta = \frac{(df/dT)T}{(d\sigma/d\theta)} \qquad (26)$$

Once again the work by Andersson and Berkyto [1] proves of value in determining the agreement between this somewhat simple picture and what is observed experimentally. Their original equation [see equation (12) above] will be modified to the absolute temperature scale:

$$S = (A\epsilon + B\epsilon^2) + (C\epsilon + D\epsilon^2)(T - 273) \qquad (27)$$

Thus from (26) and (13)

$$\eta = \frac{(dS/dT)(df/dS)T}{(d\sigma/d\theta)} = \left(\frac{10^6}{wd}\right)\frac{(dS/dT)T}{(d\sigma/d\theta)} = \left(\frac{10^6}{wd}\right)\frac{(C\epsilon + D\epsilon^2)T}{(d\sigma/d\theta)} \qquad (28)$$

From the authors' information $(d\sigma/d\theta)$ was $3\times10^{-5}$ $sec^{-1}$; $w$ was 1.5 for newsprint and 1.0 for kraft. Once again values have to be assumed for $d$ as these were not given and the same values of 0.005 and 0.008 taken before for newsprint and kraft will be assumed. Table V gives the calculated values for $\eta$ by equation (28) for a value of $\epsilon = 1\%$, i.e., $\sigma = 0.01$ and $T = 293$.

There is no direct confirmation of these figures, but Andersson, Ivarsson, Nissan, and Steenberg [2], who made an extensive study of the viscosity of the dashpot in the models for paper, make the following two statements:

1. The viscosity appears to be of the order of $10^{12}-10^{13}$ poises and the variation between different kinds of paper tested is rather small.

2. It appears that the viscous properties follow the elastic ones in this respect. The machine direction shows a much higher viscosity than the cross direction. . . . This observation corresponds to the experience that the flow properties are always pronounced in the cross direction.

Once again the simple picture of hydrogen bridges being strained and, due to their weak nature, breaking under the strain and the effects of thermal agitation appears not to contradict observations.

**TABLE V**

| | $C$ | $D$ | $\eta$, poises |
|---|---|---|---|
| Newsprint | | | |
| Machine Direction | −0.0102 | +0.0028 | $4.4\times10^{12}$ |
| Cross Direction | −0.0038 | +0.0014 | $3.1\times10^{12}$ |
| Kraft | | | |
| Machine Direction | −0.0128 | +0.0029 | $12.1\times10^{12}$ |
| Cross Direction | −0.0070 | +0.0016 | $6.6\times10^{12}$ |

The artificial nature of the dashpot, however, can be seen from the observation that according to equation (28), which appears to predict $\eta$ correctly, the viscosity *increases* with $T$. The mechanical model is then simply a mathematical artifice; a more useful approach appears to be the study of the kinetics of bond breakage under different conditions of straining, temperature, and humidity. The empirical technique adopted here[2] can only be regarded as a temporary makeshift until the kinetics of the problem are investigated by established methods of physical chemistry.

## 5. Rejoining of Broken Bonds

In studying the rates of the breaking of bonds, at least a quantitative, though not rigorous, treatment was possible on the basis of data available at present. In this section on the rejoining of bonds, not even such an approximate treatment is possible and the remarks made here are, therefore, purely speculative.

Since the hydrogen bonds are uniformly distributed in the volume occupied by the sheet when averages are taken over a microscopic volume which is large compared with a cellulose molecule, it is expected that unsatisfied bonds due to recent break will not remain long before they encounter similar ones and, since the energy barrier is small, they rejoin. In this way it is expected that, although energy is lost irreversibly insofar as the experimental determination of elastically available energy is concerned, the number of bonds formed between and within fibers should show an increase with time of rest after a severe test. A study of $r_i$ with time of rest should, therefore, indicate the rate of bond reformation. Such a study of change in $r_i$, both its decrease under strain and its increase under favorable conditions, may throw light on the mechanism and criteria of ultimate rupture.

## 6. Discussion

There are points in the theory which await elucidation.

[2] It should be noted that equations (24) to (28) inclusive and all other expressions can be derived with less empiricism if $\Delta U_2$ be allowed to equal an entropy term; $\Delta U_1$, a free energy term; and $\Delta U$, an internal energy increase in a thermodynamic equation [4]. The reason that the present empirical rather than the more satisfying thermodynamic approach was adopted was due to a doubt whether the system was in thermodynamic equilibrium.

### 6.1 *The Large Value of a*

The Morse function given in equation (3)

$$U = U_o(e^{-2a\sigma} - 2e^{-a\sigma}) \tag{3}$$

is a special form of the more general equation

$$U = \alpha r^{-n} - \beta r^{-m} \tag{29}$$

where $r$ = distance between centers of interacting atoms. Thus, since $\sigma = \ln (r/r_o)$,

$$U = \alpha r_o^{-n} e^{-n\sigma} - \beta r_o^{-m} e^{-m\sigma} \tag{30}$$

Hence,

$$\begin{aligned} f &= dU/d\sigma \\ &= \beta r_o^{-m} m e^{-m\sigma} - \alpha r_o^{-n} n e^{-n\sigma} \\ &= Be^{-m\sigma} - Ae^{-n\sigma} \end{aligned} \tag{31}$$

where $B = \beta r_o^{-m} m$ and $A = \alpha r_o^{-n} n$. Expanding,

$$f = (B-A) + (An - Bm)\sigma - \frac{(An^2 - Bm^2)\sigma^2}{2} + \frac{(An^3 - Bm^3)\sigma^3}{6} - \cdots \tag{32}$$

But since $f = 0$ when $\sigma = 0$

$$\therefore \quad B = A$$

and

$$f = A\{(n-m)\sigma - [(n^2 - m^2)/2]\sigma^2 + (n^3 - m^3/6)\sigma^3 - \cdots\} \tag{33}$$

$$= E\sigma - K\sigma^2 \tag{34}$$

where

$$E = \alpha r_o^{-m} n(n-m) \tag{35}$$

$$K = \alpha r_o^{-n} n(n^2 - m^2)/2 \tag{36}$$

But at $r = r_o$, $U = -U_o$

$$\therefore \quad U_o = \beta r_o^{-m} - \alpha r_o^{-n} = \alpha r_o^{-n}\left(\frac{n}{m} - 1\right) \tag{37}$$

and

$$U = U_o\left(\frac{m}{n-m}\right)\left(e^{-n\sigma} - \frac{n}{m}e^{-m\sigma}\right) \tag{38}$$

Thus if $m = a$ and $n = 2a$, the two expressions for $U$ in equations (3) and (38) become identical. This means that

$$U = \alpha r^{-36} - \beta r^{-18} \tag{39}$$

From this equation it is seen that the attractive component of the energy potential is inversely proportional to the 18th power of the intermolecular

distance. Normally the highest power deduced on theoretical grounds or evaluated is the sixth with an occasional seventh power (see Mark [8]). Similarly, the repulsive part is inversely proportional to the 36th power, whereas normally the 9th or the 12th power is used; the value of $n$ is, however, usually arbitrarily set and not deduced. Although Stockmayer [12] successfully treated the hydrogen bond in steam and ammonia by using a value for $n = 24$, 36 appears to be too high and is probably unprecedented. These high values are puzzling and would have been rejected as artifacts had not spectroscopic evidence been forthcoming to support the deductions from rheology.

### 6.2 *The Maximum in f*

Another moot point is connected with the fact that the Morse function predicts a maximum for $f$ at a strain equal to $(\ln 2/a)$ or $\sigma = 0.038$. This can be explained on the basis of either of two alternatives; i.e., *either* (1) the theory fails at strains approaching 0.038 and another mechanism should be sought to explain the stress-strain relationships of cellulose sheets; *or* (2) the hydrogen bond does in fact rupture at strains of 0.038 since at this and higher strains the strain proceeds to infinity at a decreasing stress. This hypothesis would form a first point in explaining rupture.

There is not sufficient evidence to support either hypothesis decisively, although there may be significance in the factual observation that paper and board which are made by the ordinary process of filtering from water and which are, presumably, principally hydrogen bonded rarely sustain a strain of 0.038, i.e., a stretch of 4%, without rupture.

### 6.3 *Cellulosic Sheets under Compression*

Finally, it should be noted that according to the theory the stress-strain curve obtained on compressing hydrogen bonded materials should be obtained directly from the tensile curve by substituting $(-\sigma)$ for $\sigma$ in equations (6*a*), (6*b*), or 7. While the predicted shape of the curve appears reasonable, this prediction awaits the availability of experimental data for proof.

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# The Catalytic Degradation and Oxidation of Cellulose[1]

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## Abstract

The thermal decomposition products of cellulose treated with various organophosphorus compounds were investigated.

The function of a fire retardant in cellulose is to favor the production of carbon and water rather than flammable tarry products which are formed in the thermal degradation of untreated cellulose. Furthermore, if the oxidation of the charred residue is directed toward the production of carbon monoxide rather than carbon dioxide, it is believed that the heat produced in this reaction would not be sufficient to sustain an afterglow when the flame has been removed.

A comparison was made between the amounts of char and tar produced and the efficiency of the retardant used. A correlation between the carbon monoxide-carbon dioxide ratio and the afterglow exhibited by treated cotton was made.

The results obtained support the theory that fire-resistant cellulose produces less flammable tars and more carbon monoxide than untreated cellulose. However, no significant differentiation as to the relative effectiveness of the various compounds investigated was possible.

It is suggested that further studies be completed on the various types of compounds exhibiting fire retardancy to provide a more general theory of fire-resistant cellulose.

A method has been described for the determination of water and nonaqueous volatile products resulting from the pyrolysis of cotton fabric. In this procedure the nonvolatile products, the char and tar, could also be determined.

The pyrolysis of seven treated samples of 8.2-oz cotton khaki cloth was studied at 200, 300, 400 and 500°C. Three of these samples were treated with fire-resistant compounds; the remaining four were padded with nonfire-resistant compounds.

A large part of the gaseous products from the pyrolysis was found to be nonaqueous. However, the data tend to support the dehydration mechanism for the action of fire-resistance compounds on cotton fabric.

## Introduction

This investigation is a part of the general study that has been carried out in this laboratory for several years on the reaction mechanism of fire-resistance compounds on cellulose.

A general theory of the reaction mechanism of fire-resistance compounds emphasizes that an effective compound should direct the thermal decomposition of cellulose toward the nonvolatile products carbon and water [2, 4].

$$(C_6H_{10}O_5)_x \xrightarrow{\Delta} x6C + x5H_2O$$

Many investigations reported in the literature have been based on the assumption that the gaseous product resulting from the thermal degradation of fire-resistant treated cellulose was mostly water vapor.

This investigation was undertaken to determine whether this assumption was valid.

## Procedure

A dried 0.5-g sample of 8.2-oz cotton khaki cloth was placed in a 6-in. Pyrex test tube and the remainder of the tube was packed with Pyrex glass

[1] Sponsored by the Office of Naval Research, Navy Department, Contract No. N8onr-506, Project No. NR-033-253.

**TABLE I. Results of the Pyrolysis Experiments**

| Cotton Cloth Padded with* | Temperature (°C) | Char (%) | Tar (%) | Water (%) | Nonaqueous Volatiles (%) | Total Volatiles (%) |
|---|---|---|---|---|---|---|
| Untreated | 250 | 93.3 | 1.8 | 3.1 | 1.8 | 4.9 |
| | 300 | 43.2 | 15.4 | 24.1 | 17.3 | 41.4 |
| | 400 | 16.6 | 44.1 | 18.4 | 21.0 | 39.4 |
| 10.9% Br-TAP monomer† (no fire resistance) | 200 | 70.6 | 4.8 | 18.2 | 6.4 | 24.6 |
| | 300 | 42.2 | 15.4 | 26.9 | 15.4 | 42.3 |
| | 400 | 33.5 | 21.7 | 26.8 | 18.0 | 44.8 |
| | 500 | 28.2 | 24.3 | 25.3 | 22.3 | 47.6 |
| 6.7% Diallyl melamine (no fire resistance) | 200 | 96.1 | 2.7 | 1.2 | 0.0 | 1.2 |
| | 300 | 44.8 | 12.3 | 22.2 | 20.7 | 42.9 |
| | 400 | 25.2 | 31.2 | 18.7 | 24.9 | 43.6 |
| | 500 | 17.0 | 37.9 | 16.5 | 28.6 | 45.1 |
| 10.1% $NH_4H_2PO_4$ | 200 | 61.4 | 3.9 | 21.9 | 12.8 | 34.7 |
| | 300 | 50.0 | 8.7 | 24.3 | 17.0 | 41.3 |
| | 400 | 42.0 | 10.7 | 22.9 | 24.5 | 47.4 |
| | 500 | 35.7 | 14.2 | 28.9 | 22.9 | 51.8 |
| 9.2% $(NH_4)_2HPO_4$ | 200 | 61.8 | 3.5 | 18.6 | 15.8 | 34.4 |
| | 300 | 49.4 | 8.5 | 29.4 | 12.7 | 42.1 |
| | 400 | 42.5 | 10.9 | 23.6 | 23.0 | 46.6 |
| | 500 | 35.6 | 10.6 | 23.6 | 30.2 | 53.8 |
| 11.2% $NaH_2PO_4 \cdot H_2O$ (no fire resistance) | 200 | 93.0 | 4.6 | 2.4 | 0.0 | 2.4 |
| | 300 | 52.6 | 9.9 | 26.4 | 11.1 | 37.5 |
| | 400 | 40.8 | 15.6 | 25.1 | 18.4 | 43.5 |
| | 500 | 34.0 | 16.3 | 25.8 | 23.8 | 49.6 |
| 10.2% $Na_2B_4O_7 \cdot 10H_2O$ (no fire resistance) | 200 | 95.6 | 2.8 | 1.6 | 0.0 | |
| | 300 | 50.4 | 11.4 | 24.9 | 13.2 | 1.6 |
| | 400 | 37.6 | 19.3 | 20.2 | 22.5 | 38.1 |
| | 500 | 30.7 | 21.3 | 23.7 | 25.2 | 42.7 |
| | | | | | | 48.9 |
| 14% $CHCl_3$-TAP polymer‡ | 200 | 64.6 | 4.1 | 27.4 | 4.2 | 31.6 |
| | 300 | 48.1 | 15.5 | 27.8 | 8.6 | 36.4 |
| | 400 | 38.7 | 16.3 | 29.6 | 15.4 | 45.0 |
| | 500 | 31.1 | 19.7 | 28.9 | 20.2 | 49.1 |

* The various percentages in this column represent the add-on of the treated cloth.
† Brominated-triallyl phosphate.
‡ Chloroform-triallyl phosphate polymer.

wool. After having been dried overnight at 110°C, the container and contents were cooled in a desiccator and weighed.

A drying tube containing 8-mesh anhydrous calcium chloride was prepared and stoppered with a one-hole rubber stopper, through which extended a short length of capillary tubing. This tube was weighed and placed in a desiccator over anhydrous calcium chloride until required in the degradation experiment.

The thermal degradation employed in these experiments was pyrolitic. For the pyrolysis the drying tube was attached to the test tube and the apparatus was placed in a furnace, which had been previously heated to the desired temperature. The furnace consisted of an aluminum block wound with resistance wire. Holes were bored in the block approximately 3 in. deep to accommodate the pyrolysis tubes. The furnace was wrapped with asbestos to minimize heat loss. The temperature was measured by means of a thermocouple inserted into a pyrolysis tube used as a blank and was controlled by a pyrometer. The sample was pyrolyzed for 90 min. The apparatus was then removed from the furnace and placed in a horizontal position in a drying oven with the drying tube extending completely out of the oven and insulated from the temperature within the oven. The test tube was dried in this manner overnight at

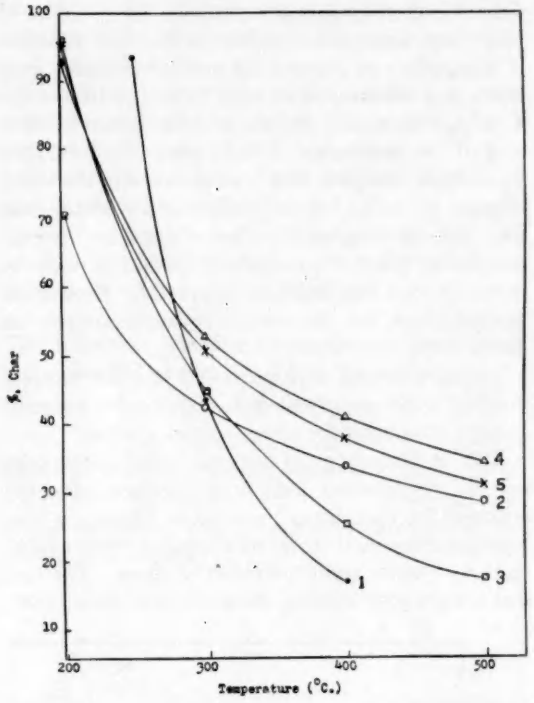



**Fig. 1A.** Char of treated samples vs. temperature. 1. Untreated. 2. Brominated triallyl-phosphate monomer. 3. Diallyl melamine. 4. Sodium dihydrogen phosphate. 5. Borax.

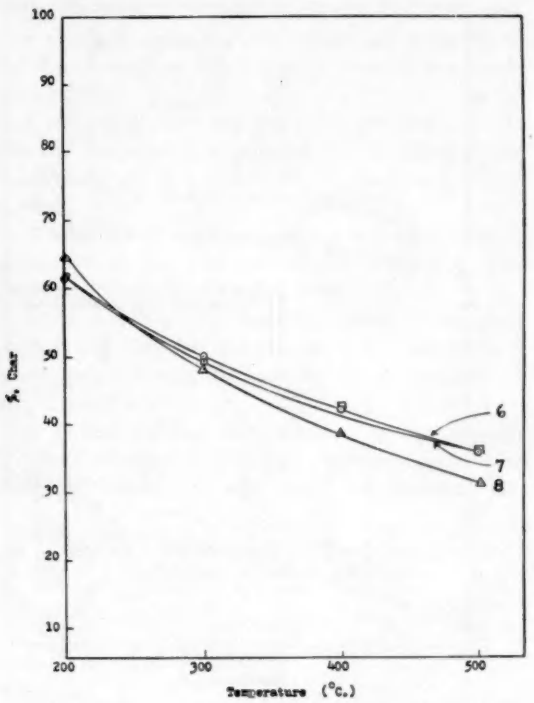



**Fig. 1B.** Char yield vs. temperature. 6. Ammonium dihydrogen phosphate. 7. Diammonium hydrogen phosphate. 8. Chloroform-triallyl phosphate polymer.

110°C in order to force into the drying tube any moisture which had collected in the glass wool during the pyrolysis. The apparatus was then allowed to cool in a desiccator and the test tube with contents and the drying tube were weighed separately. The char resulting from the pyrolysis was then removed from the tube and also weighed.

## Calculations

The difference between the weight of the pyrolysis tube before and after pyrolysis gave the amount of total volatiles produced. The difference between the weight of the sample and the sum of the weights of char and total volatiles gave the weight of tar formed collected in the glass wool. The amount of water formed in each experiment was determined by subtracting the weight of the drying tube before pyrolysis from the weight of the drying tube after pyrolysis. The difference between the weight of total volatiles and water gave the amount of non-aqueous volatile products.

## Results and Discussion

Although the primary purpose of this investigation was the study of the gaseous products from the pyrolysis of fire-resistant treated cotton, other pertinent data were collected to determine whether some correlation was possible with other phases of research in progress in this laboratory and others on the mechanism of fire-resistant treatment for cotton. The amount of char and tar formed was recorded.

The results of the pyrolysis experiments are summarized in Table I. Figures 1–4 show the data plotted against the temperature of thermal degradation. In this investigation seven treated samples were used. Four samples were padded with compounds that do not produce fire resistance and three were treated with compounds which do produce fire resistance. The brominated triallyl phosphate mono-

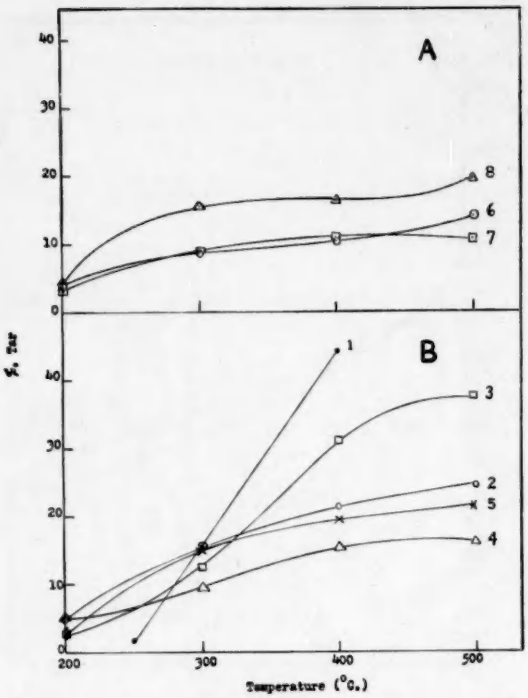



**Fig. 2.** Tar yield vs. temperature. 1. Untreated. 2. Brominated triallyl phosphate monomer. 3. Diallyl melamine. 4. Sodium dihydrogen phosphate. 5. Borax. 6. Ammonium dihydrogen phosphate. 7. Diammonium hydrogen phosphate. 8. Chloroform-triallyl phosphate polymer.

mer, diallyl melamine, sodium dihydrogen phosphate, and borax were examples of the former, and the ammonium dihydrogen phosphate, diammonium hydrogen phosphate, and chloroform-triallyl phosphate polymer were examples of the latter. The effectiveness of these treatments for fire resistance was determined by standard vertical flame tests. Of the three fire retardents used, two were of the nondurable type (the inorganic phosphates); the third was a durable type. For all samples but the control (untreated cotton khaki cloth) the previous work in this laboratory showed that pyrolytic decomposition of the untreated cotton cloth does not occur appreciably below 250°C and is virtually complete at 400°C. The pyrolysis was carried out at 200, 300, 400, and 500°C.

The data given in Table I and shown in Figures 1–4 prove that a significant amount of the volatile products from the pyrolysis of cotton khaki cloth, both treated and untreated, both fire resistant and not fire resistant, is nonaqueous. Table II emphasizes this fact by listing separately the per cent of water and nonaqueous volatiles in the total volatiles. A comparison of Figures 3*A* and 3*B* indicates generally that the compounds used for fire resistance did direct the thermal degradation of the cotton initially toward the production of more water than resulted from those samples which were not fire resistant. Figures 1*A* and 1*B* provide additional evidence that with fire-resistant samples more extensive decomposition at the low pyrolysis temperatures was obtained because less char was observed for these three samples than for the nonfire-resistant samples at 200°C.

The data shown in Figures 2*A* and 2*B* indicate that less tar formation resulted from the fire-resistant samples than from the other samples studied.

This investigation, in general, provides support for the dehydration mechanism proposed for the action of fire-resistant compounds on cotton. A fire-resistant compound serves as a catalyst for the elimination of water from the cellulose chain. The fact that a large proportion of the pyrolysis volatile prod-

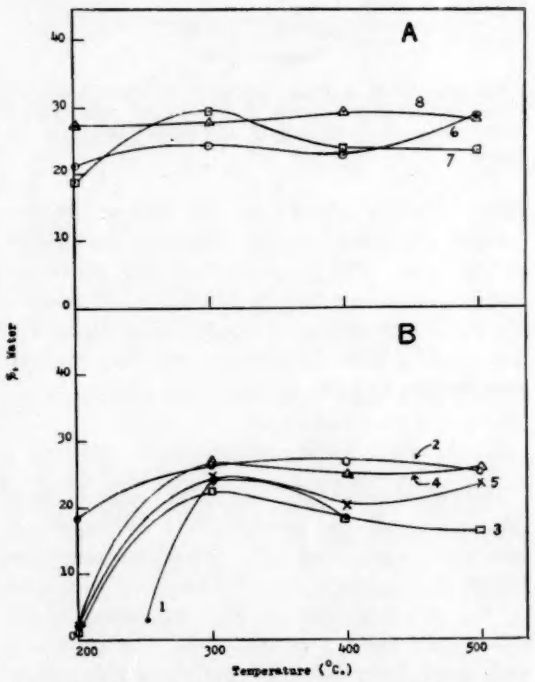



**Fig. 3.** Water yield vs. temperature. 1. Untreated. 2. Brominated triallyl phosphate monomer. 3. Diallyl melamine. 4. Sodium dihydrogen phosphate. 5. Borax. 6. Ammonium dihydrogen phosphate. 7. Diammonium hydrogen phosphate. 8. Chloroform-triallyl phosphate polymer.

ucts obtained was not water might be considered a function of the effectiveness of the compounds used as fire retardants.

The data obtained in this investigation are not considered a complete answer to problems of the mechanism of fire-resistant compounds on cotton. Additional fire-resistant preparations should be studied as to their effect on the pyrolytic volatile products. A more exact analysis of the pyrolysis products (both volatile and nonvolatile) should be completed.

## The Effect of Various Organophosphorus Compounds on the Thermal Degradation of Cellulose

The object of this investigation was to study the effects of various organophosphorus compounds on the thermal degradation of cellulose. The apparatus and experiments were designed to provide the following information:

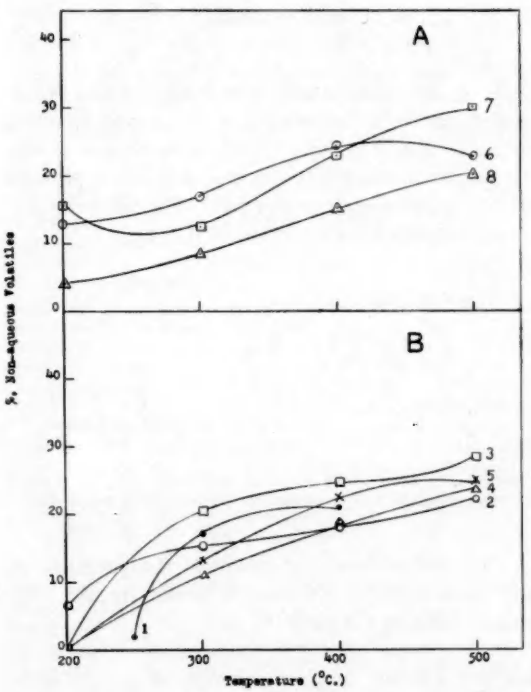



**Fig. 4.** Nonaqueous volatiles yield vs. temperature. 1. Untreated. 2. Brominated triallyl phosphate monomer. 3. Diallyl melamine. 4. Sodium dihydrogen phosphate. 5. Borax. 6. Ammonium dihydrogen phosphate. 7. Diammonium hydrogen phosphate. 8. Chloroform-triallyl phosphate polymer.

1. The amount of charred residue and flammable tars produced from the combustion and pyrolysis of cellulose treated with various organophosphorus compounds.

2. A correlation between the products of the thermal degradation of cellulose and the effect on fire retardancy of the added organophosphorus compounds.

3. The ratio of carbon monoxide to carbon dioxide produced in the oxidation of the charred residue from the pyrolysis of treated cellulose.

4. A correlation between the carbon monoxide-carbon dioxide ratio and the effect that the organophosphorus compounds have on the glow resistance of cellulose.

5. Investigation of the possibility of one or more of these compounds directing the decomposition of cellulose toward the production of less flammable tars

**TABLE II. Percentage of Water and Nonaqueous Volatiles in Total Volatiles**

| | Temperature (°C) | Water (%) | Nonaqueous Volatiles (%) |
|---|---|---|---|
| Cotton Cloth Padded with | | | |
| Untreated | 250 | 63.3 | 36.7 |
| | 300 | 58.2 | 41.8 |
| | 400 | 46.7 | 53.3 |
| 10.9% Br-TAP Monomer | 200 | 74.0 | 26.0 |
| | 300 | 63.6 | 36.4 |
| | 400 | 59.7 | 40.3 |
| | 500 | 53.2 | 46.8 |
| 6.7% Diallyl Melamine | 200 | 100.0 | 0.0 |
| | 300 | 51.7 | 48.3 |
| | 400 | 42.9 | 57.1 |
| | 500 | 36.6 | 63.4 |
| 11.2% $NaH_2PO_4 \cdot H_2O$ | 200 | 100.0 | 0.0 |
| | 300 | 70.4 | 29.6 |
| | 400 | 57.7 | 42.3 |
| | 500 | 52.1 | 47.9 |
| 10.2% $Na_2B_4O_7 \cdot 10H_2O$ | 200 | 100.0 | 0.0 |
| | 300 | 65.3 | 34.7 |
| | 400 | 47.3 | 52.7 |
| | 500 | 48.5 | 51.5 |
| 10.1% $NH_4H_2PO_4$ | 200 | 63.1 | 36.9 |
| | 300 | 58.8 | 41.2 |
| | 400 | 48.3 | 51.7 |
| | 500 | 55.8 | 44.2 |
| 9.2% $(NH_4)_2HPO_4$ | 200 | 54.0 | 46.0 |
| | 300 | 69.9 | 30.1 |
| | 400 | 50.7 | 49.3 |
| | 500 | 43.8 | 56.2 |
| 14% $CHCl_3$-TAP Polymer | 200 | 86.7 | 13.3 |
| | 300 | 76.4 | 23.6 |
| | 400 | 85.8 | 34.2 |
| | 500 | 59.0 | 41.0 |

and a greater ratio of carbon monoxide to carbon dioxide.

6. Investigation of what effect catalytic amounts of these retardants have on the fire retardancy of cellulose and comparison of this effect with a larger add-on.

A completely satisfactory mechanism for the thermal degradation of cellulose has not been substantiated, but it is known that the function of the fire retardant is to favor the production of carbon and water rather than the decomposition to flammable tarry products which are favored in the degradation of untreated cellulose.

The tars produced from treated cellulose vary only slightly in composition from the tars from untreated cellulose. They appear to be of the same composition and are fairly similar in flammability. Therefore, the main effect of a retardant is not to alter the composition or the flammability of the tar, but to reduce the yield.

Gases from treated and untreated cellulose show no appreciable change in composition and the production of carbon dioxide does not vary. These results indicate that gases have no relation to the flammability of cellulose. This conclusion must not be confused with the relation of gases to afterglow.

An analysis of the resultant char showed that it is composed of 85–90% carbon; small amounts of oxygen, hydrogen, and ash constituted the remainder. The relative efficiencies of the various fire-retarding compounds are fairly closely related to their ability to convert the cellulose at flame temperatures to large yields of this nonvolatile carbonaceous material. When 10–15% of the effective retardants are added to cotton, the carbon residue is increased from 10–40% of the original cellulose. Further addition of the retardant has little if any effect on the amount of the char produced [1].

Cellulosic materials have a tendency to exhibit a glow type of combustion after the flame has been extinguished. This afterglow is an exothermic reaction and is often more injurious than flaming itself. It is an important phase in the study of the thermal degradation of cellulose. The afterglow is caused by the oxidation of the resultant carbonaceous char. The propagation of the glow is believed to be caused by the high exothermicity of the reaction. The direction of this oxidation toward a less exothermic reaction would result in a decrease in afterglow.

The principal gases produced in the oxidation of carbon are carbon dioxide and carbon monoxide. The production of the former is a much more exothermic reaction. If the oxidation is promoted in the direction of carbon monoxide formation rather than of carbon dioxide, the heat of the reaction is reduced from 94.4 to 26.4 k/M [6].

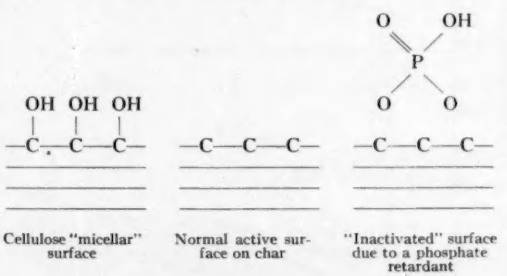
$$C + O_2 \rightarrow CO_2 \quad \Delta H = 94.4 \text{ kcal}$$
$$C + \tfrac{1}{2}O_2 \rightarrow CO \quad \Delta H = 26.4 \text{ kcal}$$

These data indicate that the first reaction is the one that sustains the glow and the second is of insufficient exothermicity to propagate afterglow after the flame has been removed.

The phosphoric acid released from the organophosphorus compounds at flaming temperatures is believed responsible for the decreased exothermic production of carbon monoxide. The mechanism favoring this reaction may involve changes in energy barriers (heats of activation) for the two reactions or it may proceed by the following reactions [6]:

$$2H_3PO_4 + 5C \rightarrow 2P + 5CO + 3H_2O$$
$$4P + 5O_2 \rightarrow 2P_2O_5$$
$$P_2O_5 + 5C \rightarrow 2P + 5CO$$

It is also possible that the phosphate may be absorbed on the active centers of the carbon, resulting in a decrease in activity. The surface sorption may be similar chemically to the graphitic acid type, such as graphitic bisulfate or fluoride. The following diagrams illustrate such a reaction [6].




Cellulose "micellar" surface — Normal active surface on char — "Inactivated" surface due to a phosphate retardant

The method used for studying the products of the combustion of cellulose is similar to the procedure used by Coppick [6].

It was found that the temperature attained by burning a fabric is approximately 500°C and complete combustion of a sample required less than 15 min. A rate of 100 cc of air per minute was sufficient for complete oxidation. The combustion reactions in this investigation were performed at a temperature of 500°C. Each sample was allowed to

burn 15 min. In order to insure complete combustion, an air flow of 180 cc/min was maintained.

The pyrolysis procedure used was similar to that described by Coppick [3] with a modified pyrolysis tube. The experimental conditions were 500°C, 20 mm of mercury, and 15 min pyrolysis time.

## Results

**TABLE III. Char-Tar Ratio of Cellulose Treated with Catalytic Amounts of Fire Retardants**

| Compound | Char (%) | Tar (%) | Char/Tar |
|---|---|---|---|
| Blank | * | 43.36 | — |
| Modified Triallyl Phosphate | 3.58 | 18.69 | 0.1904 |
| Brominated Triallyl Phosphite | 1.49 | 25.04 | .0595 |
| Brom. Modified Triallyl Phosphate | 1.49 | 24.33 | .0612 |
| Brom. bis-Allyl, *n*-Butyl Phosphate | 1.67 | 20.78 | .0803 |
| Brominated Aniline Triallyl Phosphite | 1.35 | 24.67 | .0548 |

* Impossible to recover char.

**TABLE IV. Char-Tar Ratio of Cellulose Treated with 15–25% Add-On of Fire Retardants**

| Compound | Char. (%) | Tar (%) | Char/Tar |
|---|---|---|---|
| Blank | * | 43.36 | — |
| Modified Triallyl Phosphate | 15.93 | 19.51 | 0.8165 |
| Brominated Triallyl Phosphite | 11.52 | 18.41 | .6257 |
| Brom. Modified Triallyl Phosphate | 9.55 | 16.16 | .5909 |
| Brom. bis-Allyl, *n*-Butyl Phosphate | 11.91 | 16.32 | .7297 |
| Brominated Aniline Triallyl Phosphite | 15.54 | 17.34 | .8967 |

* Impossible to recover char.

**TABLE V. Char-Volatiles and CO—$CO_2$ Ratio of Cellulose Treated with Catalytic Amounts of Fire Retardants**

| Compound | Char (%) | Char/Vols. | CO (%) | $CO_2$ (%) | $CO/CO_2$ |
|---|---|---|---|---|---|
| Blank | 7.80 | 0.0850 | 7.8 | 8.2 | 0.947 |
| Modified Triallyl Phosphate | 16.62 | .1993 | 15.4 | 4.6 | 3.348 |
| Brominated Triallyl Phosphite | 18.23 | .2229 | 8.8 | 5.0 | 1.760 |
| Brom. Modified Triallyl Phosphate | 19.58 | .2434 | 12.5 | 5.4 | 2.314 |
| Brom. bis-Allyl, *n*-Butyl Phosphate | 16.93 | .2038 | 15.8 | 5.3 | 2.981 |
| Brominated Aniline Triallyl Phosphite | 16.62 | .1993 | 15.8 | 5.4 | 2.926 |

**TABLE VI. Char-Volatiles and CO—$CO_2$ Ratio of Cellulose Treated with 10–20% Add-On of Fire Retardants**

| Compound | Char (%) | Char/Vols. | CO (%) | $CO_2$ (%) | $CO/CO_2$ |
|---|---|---|---|---|---|
| Blank | 7.80 | 0.0850 | 7.8 | 8.2 | 0.947 |
| Modified Triallyl Phosphate | 33.45 | .5026 | 7.9 | 6.0 | 1.316 |
| Brominated Triallyl Phosphite | 36.22 | .5679 | 9.0 | 6.8 | 1.550 |
| Brom. Modified Triallyl Phosphate | 32.09 | .4726 | 9.3 | 6.0 | 1.729 |
| Brom. bis-Allyl, *n*-Butyl Phosphate | 32.68 | .4854 | 12.8 | 7.4 | 1.729 |
| Brominated Aniline Triallyl Phosphite | 36.11 | .5636 | 12.4 | 7.4 | 1.610 |

## Discussion of Results and Conclusion

The combustion of cellulose treated with catalytic amounts (approximately 1%) of the retardants used in this investigation gave no indication as to the relative effectiveness of the compounds. It was demonstrated that as a group these organophosphorus compounds exhibited promise as fire retardants. The flammable tars produced by the treated samples were reduced by approximately one-half as compared to the untreated sample (Table III).

The cotton samples treated with an increased add-on ranging from 10–20% decreased the production of flammable tars by approximately 60% (Table IV). The charred residues showed a marked increase in weight as compared to the chars from samples which were treated with catalytic amounts of retardant. This increase in weight is probably caused by the decomposition products of the added retardant and would not serve as a correct indication of the efficiency of the retardant. The relative effectiveness of the various retardants was not apparent.

According to the results of Esteve and Laible [5], the brominated tri-allyl phosphate was the outstanding fire retardant in the group of compounds investigated. There was no evidence obtained substantiating this conclusion in the data obtained from the combustion experiments.

Oxidation of the char obtained from the pyrolysis of cellulose treated with catalytic amounts of retardants exhibited a marked increase in the production of carbon monoxide when compared with the char from the untreated sample (Table V). A comparison of these data and the results of the afterglow tests on fabric treated with similar add-ons showed no correlation. The treated fabric exhibited

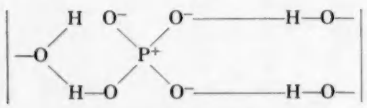
considerable afterglow, comparable to an untreated sample.

Similar results were obtained from samples treated with 10–20% add-on (Table VI). There was no correlation with similarly treated fabrics which exhibited varying degrees of afterglow.

The char-volatiles ratio was no indication of effectiveness because of the added weight of the decomposition products of the retardant.

The results obtained from these experiments provide evidence supporting the theory that flame-resistant cellulose, when compared with untreated cellulose, produces less flammable tars and an increased amount of carbon monoxide. There was no significant differentiation possible as to relative effectiveness of the various compounds investigated. This lack of correlation suggests that these methods of evaluating the relative effectiveness of other fire retardants are not conclusive.

It is suggested that studies be made as to the types of compounds exhibiting fire retardancy. A theory that should be expanded requires compounds that are capable of hydrogen bonding. If these compounds were absorbed by the cellulose fiber there is the possibility that they might combine with the hydroxyl groups and direct the degradation of cellulose toward larger, less volatile fragments, i.e., the phosphoric acid released from the organophosphorus compounds:



Hydrogen Bonding Between Phosphate and Cellulose Molecules

## Summary

1. The charred residue and flammable tars produced from the combustion and pyrolysis of cellulose treated with various organophosphorus compounds were investigated.

2. The treated cellulose produced an increase in the amount of char and a lesser amount of flammable tars when compared with an untreated sample.

3. There was no correlation between the products of the thermal degradation of treated cellulose and the relative effect on fire retardancy of the added organophosphorus compounds.

4. The ratio of carbon monoxide to carbon dioxide produced in the oxidation of the charred residue from the pyrolysis of treated cellulose was determined.

5. The treated cellulose produced an increase in the carbon monoxide-carbon dioxide ratio when compared with an untreated sample.

6. There was no correlation between the carbon monoxide-carbon dioxide ratio and afterglow of the treated samples.

7. There was no compound in the group of retardants investigated that was outstanding in directing the decomposition of cellulose toward the production of less flammable tars and a greater ratio of carbon monoxide to carbon dioxide.

8. When the retardants investigated were applied in catalytic amounts there was little effect observed on the fire retardancy of cellulose.

9. These methods, flammable tar formation and carbon monoxide-carbon dioxide ratio, for evaluating the relative effectiveness of fire retardants for cellulose are not conclusive.

10. It is recommended that further studies be completed on the type of compounds imparting fire-retardant properties when applied to cellulose in order to develop a more general theory.

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*Manuscript received March 17, 1955.*

# Letter to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

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## Electrical Resistance of Viscose Rayon at Low Temperatures

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To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

In connection with a study of the tensile properties of fibers at low temperatures [1] some measurements have been made of the electrical resistance of viscose rayon yarn in the temperature range 20°C → −60°C.

Resistance was measured using a circuit similar to that described by Hersh and Montgomery [5]. The voltage across the specimen was kept at 100 v in order to eliminate the voltage effect described by Hearle [3]. The fiber sample was similar to that used by Hearle [2] in his study of the effect of elevated temperatures on the resistance of fibers. A hundred turns of 150-den yarn were wound round a small polythene sheet which had tin electrodes fixed to two opposite edges. Good electrical contact between the electrodes and the yarn was obtained by sealing them together with a special silver paint. Fine copper lead wires were inserted between the electrodes and the polythene sheet. After conditioning to known regains, the samples were sealed between rubber sheets to avoid any change in moisture content. For reasons which need not be discussed here the measurements were made on samples of high moisture content. The sealed sample was suspended in a vessel containing a low viscosity silicone fluid which acted as a heat-transfer medium. An outer jacket contained acetone which could be cooled by the addition of solid carbon dioxide. The acetone and silicone fluid were stirred by bubbling cold carbon dioxide through them. In this way the temperature could easily be maintained constant to within ± 1°C at any temperature in the range 20°C → − 70°C. Fifteen minutes were allowed for the sample to come to equilibrium with the temperature of the silicone bath before each measurement of resistance.

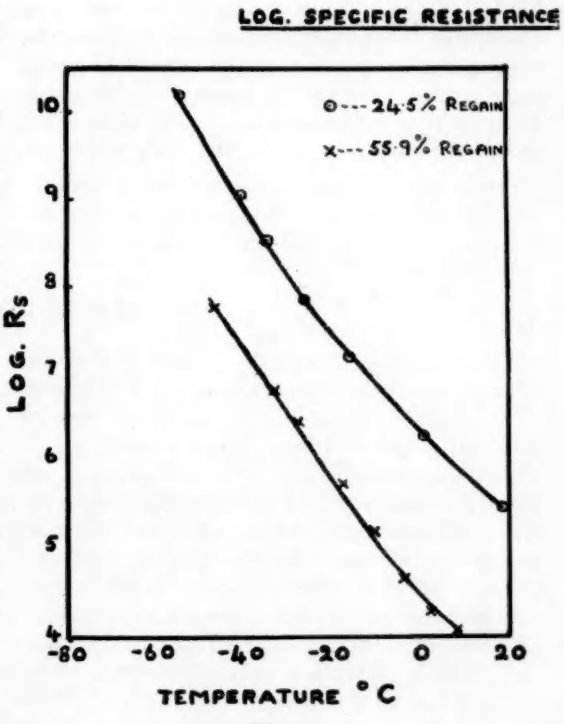


Fig. 1.

The logarithm of mass specific resistance $R_s$ is plotted against temperature in Figure 1 for samples of 24.5 and 56% regain. Mass specific resistance is defined by

$$R_s = \frac{RNw/1}{D}$$

where $R$ = the measured resistance of the sample in ohms

$N$ = the number of ends (2 × number of of turns) of yarn

$w/1$ = the mass/unit length of the yarn in g/cm

$D$ = the distance between the electrodes

$\text{Log}_{10}\ R_s$ increases with decreasing temperature according to a nearly linear relation. This result is similar to Hearle's [2] observations at higher temperatures and in fact the empirical equation which Hearle derived for his results (covering the temperature range 20°C to 100°C) fits the present results at the lower regain reasonably well.

The results presented here are too few to justify any discussion, but it is interesting to note that the curves are similar at both regains. Preston and Nimkar [6] have shown that in viscose rayon only moisture in excess of 38% regain can be frozen, the freezing point depending on the amount of excess water present. Thus in the sample of 24.5% regain no moisture is frozen even at − 60°C while in the sample of 56% regain some of the water will freeze. It is generally accepted that the mechanism of conduction of electricity through textiles is ionic, the ions travelling along water paths. Hearle [4] has suggested that at high moisture contents the main limitation to conduction is due to a viscous drag on the ions. Therefore it might be expected that the freezing of the water, which would introduce a sudden rise in the viscose drag, would cause a sudden rise in the electrical resistance. The present results, however, indicate that the conduction is independent of the state of the water.

### Acknowledgments

Thanks are due to Mr. Cusick of the Department of Textile Industries for the use of his apparatus and for his assistance in the measurements. Also to Dr. Hearle for his valuable advice.

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# INDUSTRIAL SECTION

# Studies on Spinning Rings and Travellers

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## Introduction

In this report, various characteristics of a spinning ring and traveller are mainly experimentally surveyed. Part I covers experimental methods, which include static tests and dynamic tests. Part II deals with friction and wear.

As for working characteristics, friction and wear are important, and they are surveyed in a testing machine and a spinning machine. Working characteristics depend on static characteristics and working conditions. A relationship between them has been experimentally discovered and is partly described in the form of experimental formulas. Compared with general machine parts, a ring and traveller are subjected to severe working conditions (e.g., speed: 10–30 m/sec; load: 50–200 g). Therefore, frictional and wearing phenomena may also be extraordinary and interesting.

Sample rings, shown in Table I, are made in Japan, except No. 5, which is made in the U. S. A.

**TABLE I. Sample Rings**

| Classification | Size | Description |
|---|---|---|
| 1. Polished | 41 mm (1⅝ in.) | Case hardened, polished |
| 2. Parkerlized | 41 mm (1⅝ in.) | Case hardened, granular phosphate coated or parkerlized |
| 3. Granulated | 41 mm (1⅝ in.) | Case hardened, chemically granulated |
| 4. Nitrized | 41 mm (1⅝ in.) | AlCr steel, granular nitrized |
| 5. U. S. A., polished | 47.5 mm (1⅞ in.) | U. S. A., polished |
| 6. Oil-less | 45 mm (1¾ in.) | Porous, made by powder metallurgy and permeated with mineral oil |

Sample travellers are G-1 (nearly 58 mg weight), G-1/0 (52 mg), and G-5/0 (32 mg), which are made in Japan, and 8 grain (52 mg) which is made in the U. S. A.

"Size" denotes the inner diameter of a ring frange. The width of the frange is 4.0 mm, except No. 5, the frange of which is 3.7 mm wide.

# I. Experimental Methods

## A. Static Tests

### 1. *Circularity of Rings*

The Universal measuring microscope[1] gives an accurate result, but it is unsuitable for rapid testing.

The direct measurement of diameter deviation by a dial gauge is shown in Figure 1. A ring laid upside down on a fixed bed is guided by fixed roller $A$ and movable rollers $B_1$ and $B_2$, which are held together by two pairs of equal links, $AB_1 = AB_2$ and $B_1C = B_2C$, and which rotate around $A$; the ring revolves slowly, pulling thread $T$. Pin joint $C$ is guided by a sleeve and pressed by a spring to $A$. The ring is contacted by lever $L$ at point $P$, so that a displacement of $P$ in the direction of $AP$ is nearly equal to diameter deviation.

The displacement of point $P$ is transmitted to a dial gauge by lever $L$. This apparatus has an accuracy of nearly 0.02 mm in the ordinary state and can be applied to a symmetric ring about the center (elliptic, square, etc.) but not to an unsymmetric ring (for an example, equal-diameter warped).

As shown in Figure 2, experimental results of both methods are nearly the same, and the whole distribution of diameter deviation is generally elliptic. Accordingly, the direct measurement by a dial gauge can be applied to spinning rings.

[1] Manufactured by Genevoise Co., Ltd., Switzerland.

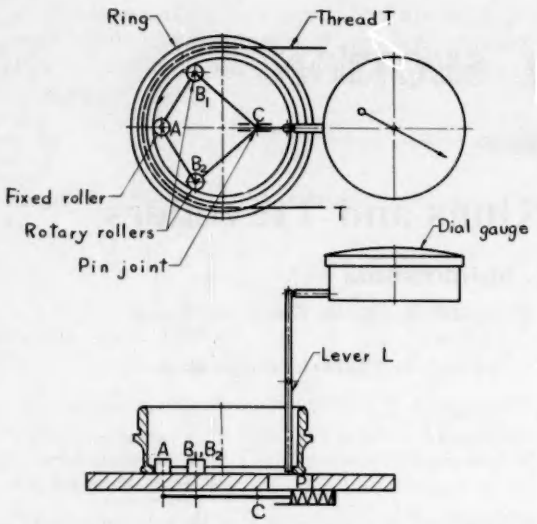



**Fig. 1.** Schematic diagram of measuring the diameter deviation of a ring by a dial gauge.

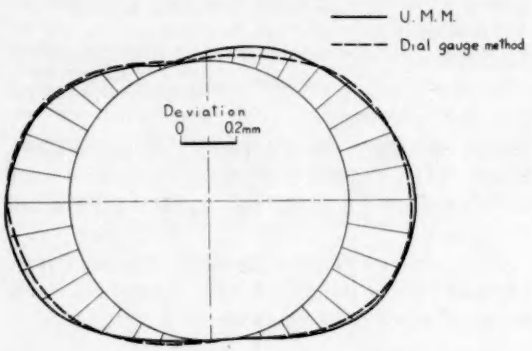



**Fig. 2.** Circularity of a No. 1 polished worn ring.

## 2. *Hardness*

Hardness distribution in a carefully finished section of a ring frange is measured at intervals of nearly 0.1 mm under a 50 g measuring load by a Micro Vickers hardness tester.[2] Experimental results are shown in Figure 3. On a traveller surface, hardness is measured alike under a 50 g load.

## 3. *Surface Profile*

The contact surface profiles of a ring and traveller are recorded on sensitive paper by a surface profile tester, which is illustrated in Figure 4. As for a ring, on a fixed bed inclined for an investigated surface of the ring to be level, the ring is laid upside down, contacted by a fixed guide, and revolves very slowly, pulled by a thread. Therefore, a contact needle moving up and down envelopes the surface profile at the constant distance inside the inner frange edge.

[2] Manufactured by Akashi Seisakusyo Co., Ltd., Japan.

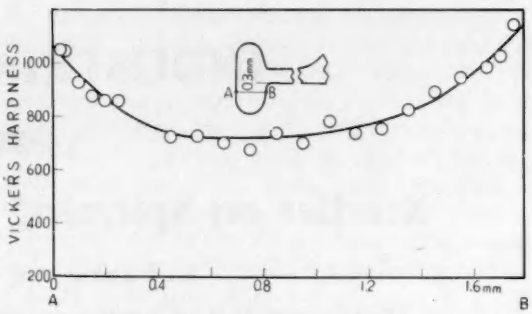



**Fig. 3.** Hardness distribution on a section of No. 1 polished ring's frange.

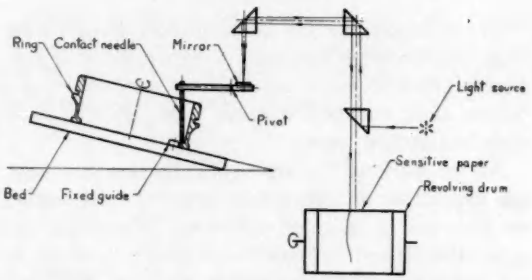



**Fig. 4.** Schematic diagram of the surface profile tester.

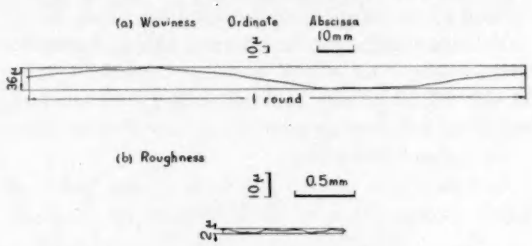



**Fig. 5.** Surface profile of No. 4 nitrized new ring.

Waviness is recorded by a round needle of nearly 0.5 mm peak radius under a 10-g contact pressure,[3] and enlarged 250 × in ordinate (height) and 1.5 × in abscissa (circumference). So a scale ratio of ordinate divided by abscissa is 167.

Roughness is recorded by a sharp needle of nearly 10 $\mu$ peak radius under 2 g contact pressure, and

[3] Measuring condition follows the Japanese Industrial Standard (JIS B0601 Explanation).

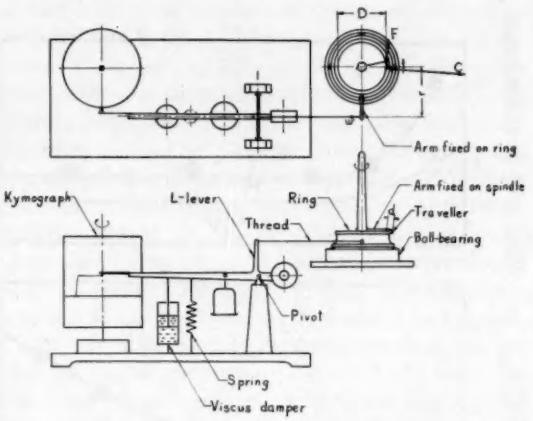



**Fig. 6.** Schematic diagram of the friction tester.

enlarged 1000 × in ordinate and 50 × in abscissa, so the scale ratio is 20.

Accordingly, the recorded roughness and waviness represent envelopes by spheres of 10 $\mu$ and 0.5 mm radius. Roughness in radius direction is recorded by moving the ring in radius and by the contact of the ring with the sharp needle.

A traveller is grasped by a chuck and moved in a longitudinal direction and width, and its roughness is recorded alike on a ring.

As an example of the recorded curve, No. 4 nitrized ring's profile is shown in Figure 5.

## B. Dynamic Tests

### 1. *Friction*

The measuring apparatus shown in Figure 6 is a self-recording type friction tester. A ring is supported by a ball-bearing, in which friction is less than 2% of the friction between ring and traveller. Frictional moment is supported by an arm fixed on the ring and balanced with spring force by an L-lever. The L-lever has a great mass and an effective viscous damper, and so the natural frequency of the L-lever is very low—nearly 2.5 cycle/sec, so the kymograph of friction indicates the mean frictional force.

In a test, a traveller is driven by a thread loop connected with an arm fixed on a spindle blade, observed through a stroboscopic,[4] and kept in the same conditions as in spinning. In spinning, where a traveller is driven by a ballooning thread, the friction is measured alike and compared with the friction in test. Rings and travellers are washed in gasoline.

Now

$m$ = Traveller weight (g)
$n$ = Spindle speed (rev/min)
$w$ = Balancing force at an arm fixed on a ring (g)
$r$ = Arm length of ring (cm)
$D$ = Ring inner diameter (cm)
$d$ = Traveller inner diameter in long axis (cm)
$g$ = Gravity constant (cm/sec$^2$)
$C$ = Centrifugal force acting on a traveller (g)

Expressions of frictional characteristics are

$F$ = Frictional force (g)
$M$ = Frictional moment (g cm)
$\mu$ = Frictional coefficient
$W$ = Frictional power (g cm/sec)

These are expressed as the following functions of $w$

$$F = (2r/D)w \tag{1}$$

$$M = rw \tag{2}$$

$$\mu = [3600rg/\pi^2 D(D + d)mn^2]w \tag{3}$$

$$W = (\pi rn/30)w \tag{4}$$

Maximum error of $\mu$ is nearly 3%, including the error caused by the friction in the ball-bearing.

### 2. *Contact Continuity*

In order to determine contact continuity of a traveller and a ring while they are in motion, variation of contact is transferred into variation of electric current by forming an electric circuit containing the contact resistance between ring and traveller. Electric current is recorded by an electromagnetic oscillograph, and its mean value is measured by an ammeter.

According to Bowden [3], the contact local part becomes plastic deformation, and the contact resistance is given by Maxwell [5]. Hence, the following formula is obtained for the circuit containing the contact of ring and traveller shown in Figure 7*a*

$$i = 1500/(0.0374P^{-\frac{1}{2}} + 53.8) \tag{5}$$

where

$i$ = Current (ma)
$P$ = Contact pressure (g)

As shown in Figure 7*b*, which is a diagram of the above equation, this apparatus can show whether a traveller contacts with a ring or separates from it,

[4] By "Strobotac," manufactured by General Radio Co., U. S. A. Its flashing time is 5–10 × 10$^{-6}$ sec.

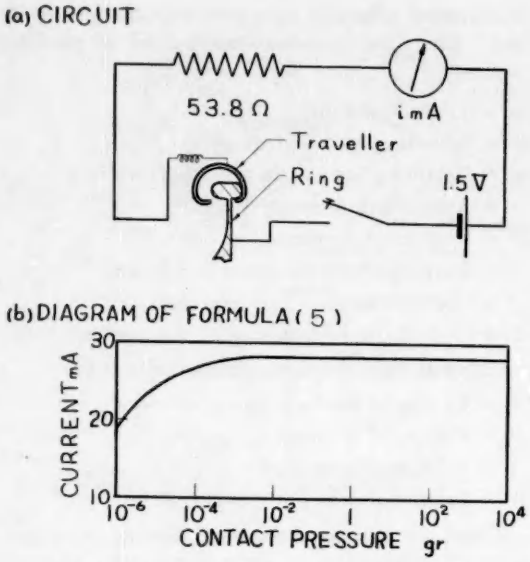



**Fig. 7.** Contact continuity of ring and traveller.

but it cannot measure the contact pressure or its area. With $c$ as

$$c = (i/i_{max}) \times 100 \qquad (\%)$$

and with $i_{max}$ as the current when contact resistance is zero ohm, $c$ may denote metallic contact continuity of traveller and ring.

### 3. *Wear*

As with friction, the wearing test is made on the tester and on the spinning. The driving method of a traveller and washing samples are all the same in friction. On the tester, a traveller is kept on constant constraint, and a rapid testing is made by vanishing a ballooning tension acting on a traveller. The purpose of the rapid testing is to keep the constant constraint condition, quicken the wearing speed, and simplify the testing. The amount of wearing is measured by a chemical balance, which has an accuracy of nearly 0.3 mg. In this report, wear characteristics are expressed mainly by a time rate of wearing, for the sake of practical convenience. An example of wear progress on the tester is shown in Figure 8.

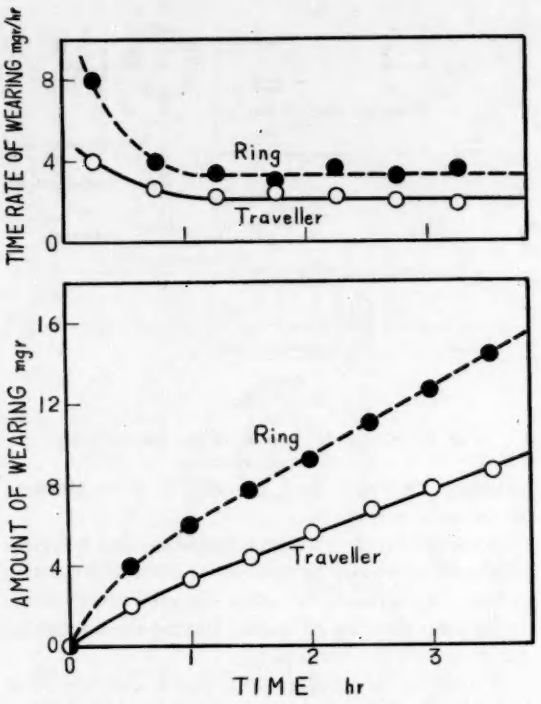



**Fig. 8.** Wear progress of ring and traveller in test. (No. 1 polished ring with G-1 traveller at 26°C, 79% R. H., and 11,000 rpm.)

At first, the time rate of wearing is great, and so-called initial wearing appears a little, but it is slighter than at the other stages of general wearing. Soon the time rate of wearing becomes constant and wear progress almost perfectly proportional to time. The time rate of wearing, including the initial wearing, is thus determined. In the wearing test, dispersion of the measured values is considerably larger than in the friction test.

# II. Friction and Wear of Rings and Travellers

## A. Physical Properties of Rings and Travellers

### 1. *Circularity of Rings, before and after Wear*

Figure 9 shows distribution of the diameter deviation on several rings. Generally speaking, spinning rings are elliptic, with the maximum diameter deviation less than 0.1 mm before wear and 0.05–0.3 mm after.

### 2. *Hardness before and after Wear*

a. *Rings.* Hardness distribution in the interior of a ring frange is shown in Figure 10.

The surfaces, *A* and *B* in the figure, are as hard as 800–1100 in V. H. (Vickers hardness), but the interiors are as soft as 350–700 V. H. Hardness difference between surface and interior is 350–570 V. H. Hardness distribution in the section varies fairly considerably according to materials and treatments. On several rings, the surface layer has considerable hardness gradient in the depth direction, which rarely exceeds 100 V. H./0.1 mm, which is undesirable from the standpoint of durability (wearproofness) and of preserving the life of the ring. Mean hardness gradient in a 0.0–0.3 mm depth is shown in Table II.

As the table shows, hardness gradient on the nitrized ring is the highest, 110 V. H./0.1 mm. On the contrary, on the U. S. A. polished ring it is the lowest, 15 V. H./0.1 mm. Interiors of granulated ring, nitrized, and U. S. A. polished are softer than those of polished ring and parkerlized ring.

On a ring having a great hardness gradient in the hardened surface layer, the worn surface grows softer as wearing advances. Consequently, the time rate of wearing of both ring and traveller increases with their working time, as shown in Figure 11.

In this figure, ring wearing of 200 mg corresponds approximately to a surface layer 0.15 mm thick. Therefore, hardness difference is nearly 150 V. H. according to the previous experimental result, so that the time rates of wearing are about 1.6 times. Therefore, experimental results of wear are converted into the original state of the ring, considering the surface hardness change by wearing.

b. *Travellers.* Hardness distribution on a traveller surface measured by the above-mentioned method is shown in Figure 12. In this figure, distribution in the longitudinal direction, I, II, . . . , is uniform at 500–650 V. H. But in the width direction—*A* to *B* in the figure—it is irregular. The reason, perhaps, is that the traveller is made uniform in the longitudinal direction during production.

3. *Profiles before and after Wear*

a. *Waviness of rings.* As shown in Figure 5, waviness of new rings is approximately a sine wave,

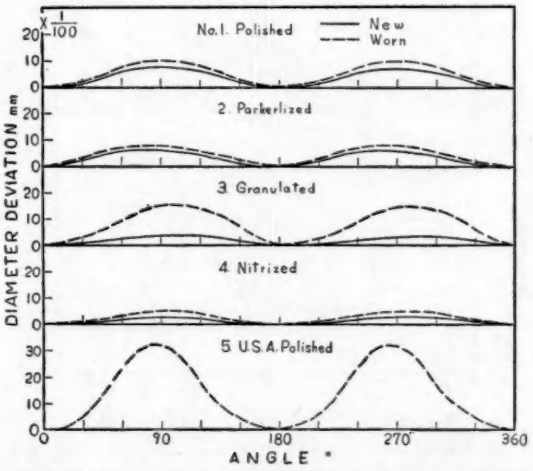



**Fig. 9.** Distribution of the ring diameter deviation before and after wear, measured by dial gauge method.

**TABLE II. Hardness Gradient in a 0.0–0.3 mm Depth, V.H./0.1 mm**

| | Ring | Upper (*A*) | Lower (*B*) | Mean |
|---|---|---|---|---|
| No. 1 | Polished | 90 | 70 | 80 |
| 2 | Parkerlized | 90 | 75 | 80 |
| 3 | Granulated | 50 | 0 | 25 |
| 4 | Nitrized | 100 | 120 | 110 |
| 5 | U. S. A., polished | 0 | 30 | 15 |

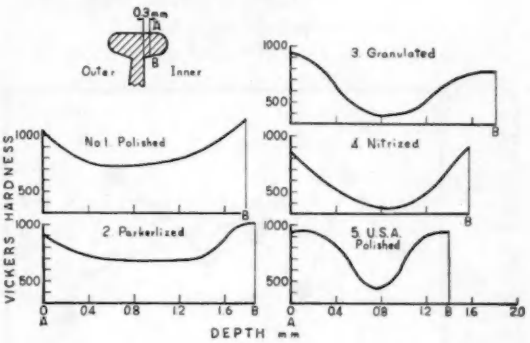



**Fig. 10.** Hardness distribution on a section of various ring's frange.

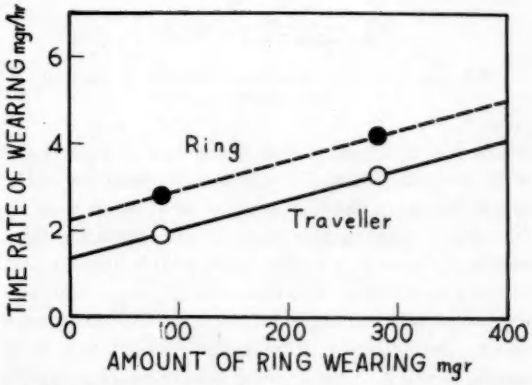



**Fig. 11.** Influence of hardness change of worn ring surface on wearing. (No. 1 polished ring with G-1 traveller at 28°C, 76% R. H., and 9000 rpm.)

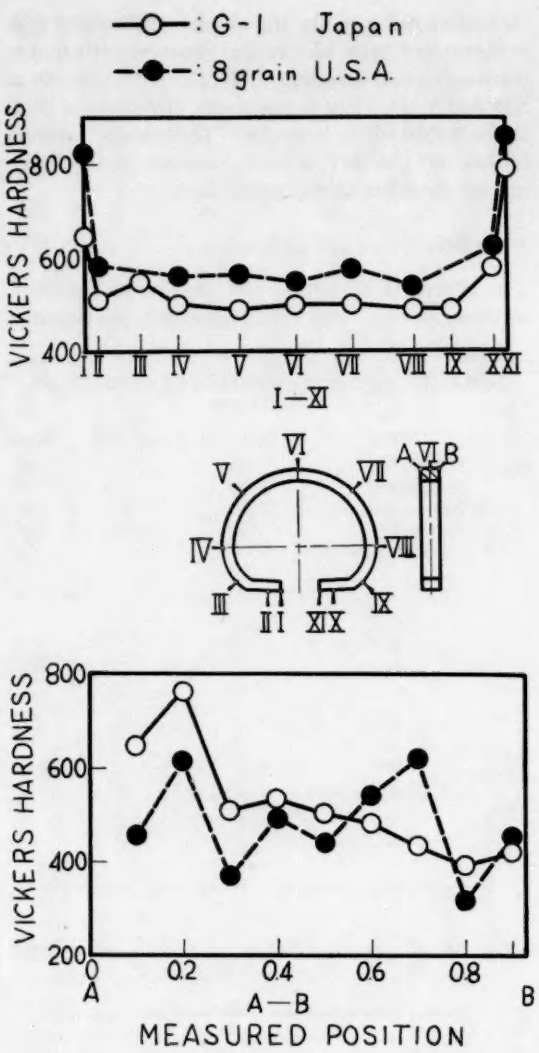



**Fig. 12.** Hardness distribution on the surfaces of new travellers.

which has a period of one round and is superposed with irregular waves of a shorter period and of a lower height. The fundamental sine wave may be because an approximate plane of path contacted by a needle inclines at a slight angle to the upper plane of the ring frange. Maximum height $H_{max}$, which is the height between upper contact line and lower, may denote the accuracy of a frange section, and it is nearly 10–40 $\mu$. As wearing advances, $H_{max}$ gradually decreases. Figure 13*a* is an example.

After long use, some rings indicate the wavy waviness shown in Figure 13*a*. Wavy worn rings generally have an almost constant pitch, 4–7 mm, and a tall wave height. Maximum height of a wave amounts to 100 $\mu$. On wavy worn rings, hardness gradient in a depth direction in the surface layer is great, and hardness difference between peak and bottom of a wave reaches nearly 100 V. H. On a ring having a small hardness gradient, as, for example, a U. S. A. polished ring, wavy wearing is

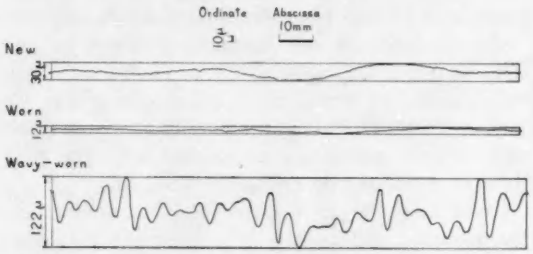



**Fig. 13a.** Waviness of No. 2 parkerlized rings before and after wear.

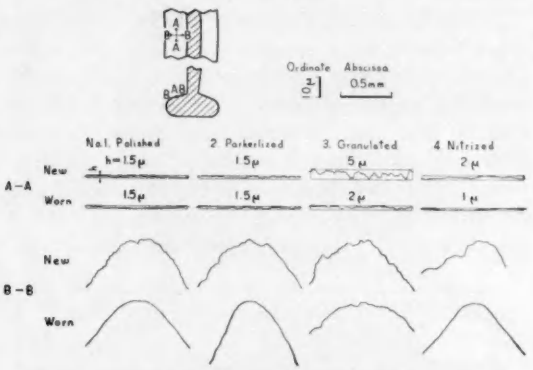



**Fig. 13b.** Roughness of rings before and after wear.

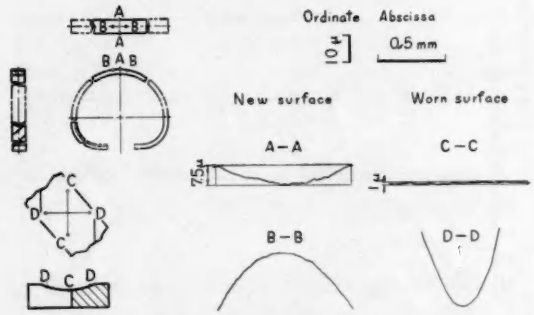



**Fig. 13c.** Roughness of a traveller before and after wear.

scarcely noticeable. Hardness gradient may have a close relationship with wavy wearing.

b. *Roughness of rings.* Recorded results are shown in Figure 13*b*. A granulated new ring has a similar maximum height, $H_{max}$, of nearly 5 $\mu$ in an interval of 1.0 mm both in the circumference direction and in radius, and so has a nondirectional granular surface. On the other hand, a new nitrized ring has a directional granular surface in circumference, because $H_{max}$ is larger in radius than in circumference, and this may be caused by the grinding effect. Tested surfaces of polished and parkerlized new rings are slightly directional in circumference. A worn ring is smooth both in frictional and rectangular directions. Generally, a worn surface is nondirectionally smooth.

c. *Roughness of travellers.* As shown in Figure 13*c*, a traveller surface is rougher in width than in longitude. This may be because the material for the traveller is produced by drawing and made uniform in a longitudinal direction. This, in turn, may have something to do with the above-mentioned hardness irregularity in width. As with rings, a worn surface of a traveller is nondirectionally smooth.

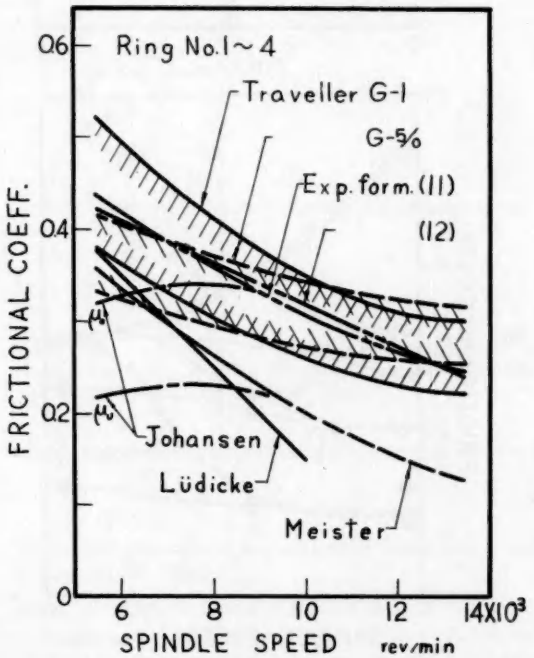



**Fig. 14.** Frictional coefficient versus spindle speed. Experimental results on worn fitted rings Nos. 1-4 in test, experimental formulas for these rings with G-1 traveller, and the results by other authorities.

## B. Spinning and Simulated Spinning Tests

### 1. *Friction*

a. *General characteristics.* Experimental results of the various rings in test generally show that frictional force $F$, moment $M$, and power $W$ increase with spindle speed $n$ and are nearly proportional to traveller weight $m$, but that frictional coefficient $\mu$ decreases with $n$ and has little to do with $m$. Figure 14 shows a $\mu$-$n$ diagram measured on the tester. On various worn fitted rings, frictional coefficient $\mu$ is almost independent of static characteristics of rings —materials, surface treatments, sectional figures of ring frange, forms of traveller, etc.—but is mainly dependent on working conditions—spindle speed, lubrication, etc. Figure 14 shows also that the measured value of $\mu$ is nearly equal to, or exceeds, Lüdicke's experimental formula (1881) $\mu = 0.65 - 0.00005n$ [7], the experimental value by Meister [6], and the calculated values $\mu^o$ at cop corn top, $\mu^u$ at cop corn base by Johansen [4].

In test, frictional force $F$ increases linearly with spindle speed $n$ on most rings, as shown in Figure 15. Therefore, the following experimental formula is obtained

$$F = an + b \tag{6}$$

where

$a$ = Experimental constant (g min/rev)
$b$ = Experimental constant (g)

In a test,

$$a = (4 - 10) \times 10^{-3} \quad \text{(g min/rev)};$$
$$b = -(10 - 60) \quad \text{(g)}$$

Accordingly,

$$M = D(an + b)/2 \tag{7}$$

centrifugal force $C$ acting on a traveller

$$C = k \cdot n^2; \qquad k = 2\pi^2 m(D + d)/60^2 g$$

Hence

$$\mu = \frac{a}{k}\frac{1}{n} + \frac{b}{k}\frac{1}{n^2} \tag{8}$$

$$W = adn^2 + bdn, \qquad d = \pi D/60 \tag{9}$$

As a mean value of experimental results of worn fitted rings ($1\frac{5}{8}$ in.) with G–1 travellers in a test

$$a = 0.006 \quad \text{(g min/rev)};$$
$$b = -13 \quad \text{(g)} \tag{10}$$
$$F = 0.006n - 13$$

Hence equation (8) is

$$\mu = 3950/n - 8560 \cdot 10^3/n^2 \qquad (k = 1.52 \times 10^{-6} \text{ g min}^2/\text{rev}^2) \tag{11}$$

as an approximate straight line

$$\mu = 0.55 - 0.000023n \qquad (12)$$

Experimental formulas (11) and (12) are shown in Figure 14.

When rings and travellers are washed in gasoline, the kymograph of friction is a one-step type. If the samples are spread with a lubricant, the kymograph is mostly a two-step type, as shown in Figure 16. The early step transfers to the last step after a length of time. The frictional coefficient at both steps is shown in the figure. Lubrication is considered to be in the state of boundary lubrication, where solid friction and fluid exist together. Accordingly, the reduction of friction by lubricants may have a relation to the adhesion of lubricants to the metallic surface. Considering the chemical structure of the lubricants, the oiliness is

castor oil > mineral oil > silicone oil

The experimental results agree with this. If spread, lubrication does not last long. At the high speed, friction on an oil-less ring, which is porous and permeated with mineral oil, is less than friction on an ordinary ring spread with a lubricant. Lubrication of the oil-less ring lasts as long as a lubricant exists on the frictional surface.

Experimental results in a fine spinning machine are shown in Figure 15. Frictional force $F$ in spinning is nearly half of what it is in a test, and experimental formulas (6), (7), and (9) are applicable to spinning. If friction experimental coefficient $\alpha_f$ denotes a quotient of frictional force in a test divided by the frictional force in spinning, $\alpha_f$ on most rings is generally independent of the spindle speed and nearly equal to 2. Experimental constant $a$ is $(3 - 6.5) \times 10^{-3}$ (g min/rev), and $b$ is $-(10 - 40)$ (g). As a mean value of experimental results when 20's cotton yarn is spun on 41 mm 1⅝ in.) various fitted rings and a G-1 traveller (58

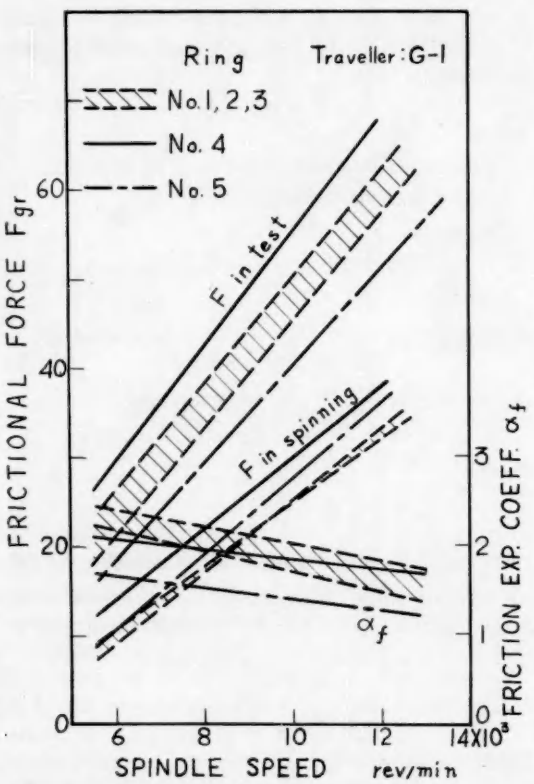



**Fig. 15.** Spindle speed versus frictional force of worn fitted rings in test and in spinning.

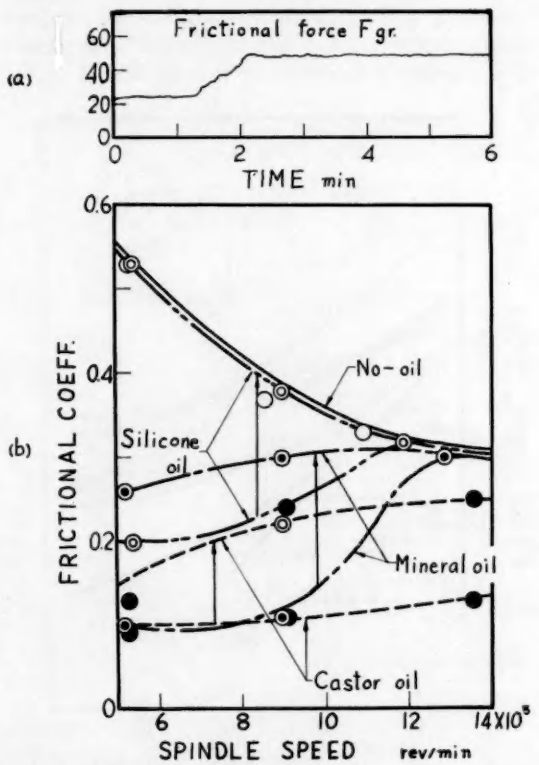
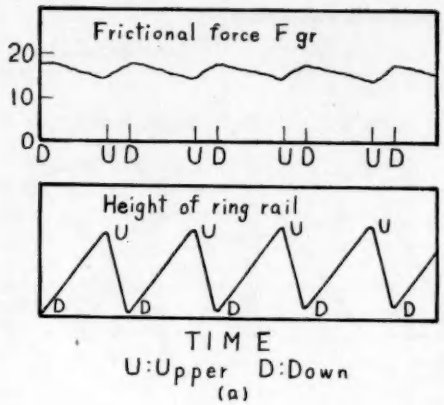



**Fig. 16.** Effect of lubricants on friction. (No. 1 polished ring with G-1 traveller in test) *a*, Kymograph spread with silicone oil at 9000 rpm. *b*, Diagram of frictional coefficient versus spindle speed.



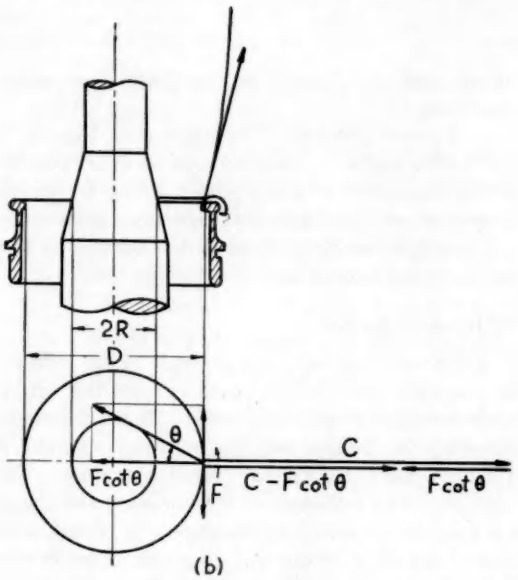




**Fig. 17.** Variation of frictional force in spinning. *a*, Kymograph during spinning 20's cotton with No. 1 polished ring and G-5/0 traveller at 10,900 rpm.

mg), the following experimental formula is obtained

$$F = 0.004n - 10 \qquad (13)$$

The above-mentioned experimental constants $a$ and $b$ indicated in Table III.

In spinning, variation of frictional force in a chase —for example, in Figure 17, nearly ± 13%—is explained by the following formula. In Figure 17*b*

$$F = \mu(C - F\cot\theta)$$

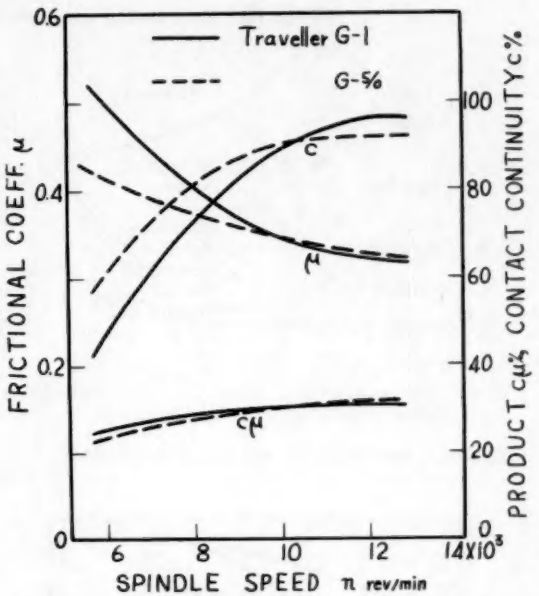



**Fig. 18.** Effect of spindle speed on contact continuity $c$, frictional coefficient $\mu$, and the product $c\mu$. (No. 1 polished ring with G-1 and G-5/0 traveller).

Hence

$$F = C/(1 + \mu\cot\theta); \qquad \theta = \sin^{-1} 2R/D \qquad (14)$$

Variation of $F$ by the calculation is ± 12.5% for the above example.

As mentioned above, frictional characteristics of worn fitted rings finished by different surface treatments are similar both qualitatively and quantitatively, but frictional characteristics of new rings fairly depend on the surface properties. In an early fitting period, friction of a polished and directional surface ring is larger than that of a granular and nondirectional one.

Under severe conditions—especially at a high speed—the influence of frictional heat is great, and a local part of the traveller which contacts a ring is annealed by the frictional heat, causing rapid progress in wearing.

### 2. *Contact Continuity*

*a. General characteristics.* As shown in Figure 18, contact continuity $c$ generally increases with spindle speed $n$; that is, contact is more continuous at a high speed than at a low. As mentioned before, frictional coefficient $\mu$ decreases with spindle speed

**TABLE III. Experimental Constants in Friction Experimental Formulas (6)–(9)**

| | | | | In Test | | In Spinning | |
|---|---|---|---|---|---|---|---|
| | Ring | Lubricant | Traveller | *a* | *b* | *a* | *b* |
| No. 1. | Polished | No oil | G-1 | $6.5 \times 10^{-3}$ | −10 | $4.0 \times 10^{-3}$ | −10 |
| | | | G-5/0 | 4.0 | −10 | — | — |
| | | Mineral oil | G-1 | 10.0 | −60 | — | — |
| 2. | Parkerlized | No oil | G-1 | 6.0 | −10 | 3.5 | −10 |
| | | | G-5/0 | 4.0 | −10 | — | — |
| | | Mineral oil | G-1 | 9.0 | −50 | — | — |
| 3. | Granulated | No oil | G-1 | 6.5 | −15 | — | — |
| | | Mineral oil | G-1 | 7.0 | −35 | — | — |
| 4. | Nitrized | No oil | G-1 | 6.0 | −10 | 3.5 | −10 |
| | | Mineral oil | G-1 | 9.0 | −50 | 4.0 | −15 |
| 5. | U. S. A., polished | No oil | G-1/0 | 5.0 | −10 | 4.0 | −10 |
| | | | 8 grain | 5.5 | −15 | 4.3 | −15 |
| | | Mineral oil | G-1/0 | 6.0 | −25 | — | — |
| | | | 8 grain | 6.0 | −25 | — | — |
| 6. | Oil-less | Self-lubricated | G-1 | 4.0 | −15 | 3.0 | −15 |

Washed in gasoline. In spinning, 20's cotton yarn.

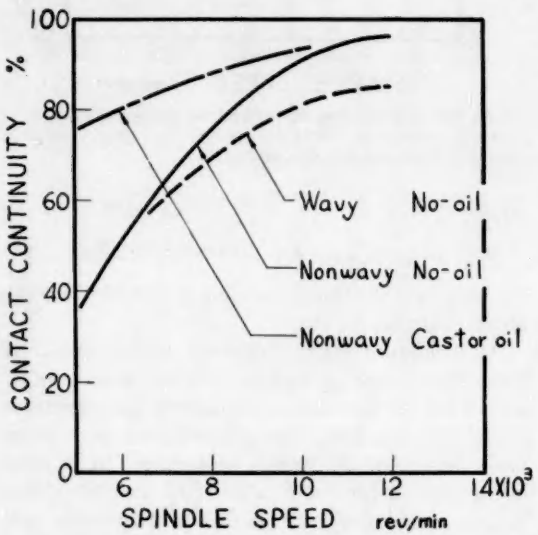



**Fig. 19.** Effect of the wavy wearing and lubricants on contact continuity. (No. 1 polished ring with G-1 traveller).

$n$, and contact continuity $c$ increases with $n$. Here, constancy of product $c\mu$ is found by experimental results. For an example, the experimental result of a No. 1 polished ring on the tester is shown in Figure 18. Product $c\mu$ is nearly constant and 20–30%. Under the other conditions the product is nearly constant.

Generally, frictional coefficient $\mu$ and contact continuity $c$ depend remarkably upon the spindle speed, but product $c\mu$ hardly depends upon the spindle speed and is approximately constant. In other words, frictional coefficient $\mu$ may be the function of contact continuity $c$.

*b. Factors affecting.* As shown in Figure 19, lubricated contact is more continuous than nonlubricated, especially at a low speed. The higher the degree of oiliness, the more continuous the contact. On a wavy worn ring, contact is less continuous than on a nonwavy worn ring at a high speed.

### 3. *Wear Behavior*

*a. Factors affecting.* An example of the influence of humidity and spindle speed on wearing on the tester is shown in Figure 20. The influence of humidity is effective for ring wearing, specially at the high speed, but not for traveller wearing. This may be due to activation of worn surface and chemical reaction promoted by moisture. A certain position of the worn surface of a ring intermittently contacts the traveller and almost touches moisture, so the chemical reaction takes place easily. High speed promotes the activation of the worn surface, and high humidity speeds up the chemical reaction. But the worn surface of the traveller continuously contacts the ring and scarcely touches moisture, so the chemical reaction hardly occurs. Wearing of both ring and traveller increases considerably with the spindle speed.

Figure 21 is a semilogarithmic diagram, in which the time rate of wearing is on a logarithmic scale and the spindle speed is on an ordinary scale. The time rates of wearing increase linearly with the spindle speed both in test and in spinning. Accordingly, the time rate of wearing is represented by the following

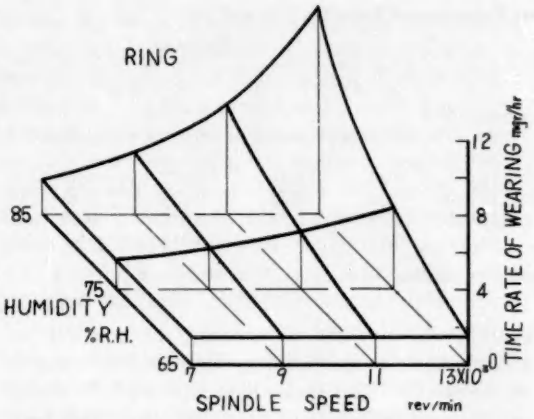



**Fig. 20a.** Cubic diagram of wearing of ring versus spindle speed versus humidity. (No. 1 polished ring with G-1 traveller at 25–29°C).

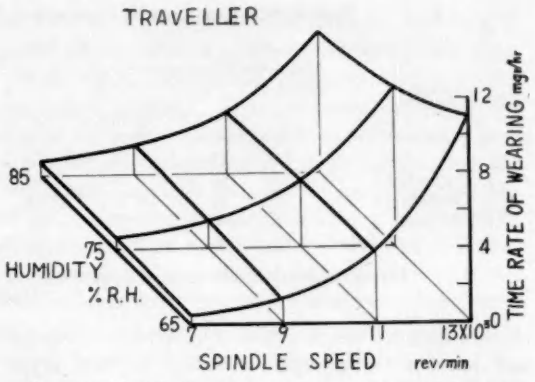



**Fig. 20b.** Cubic diagram of wearing of traveller versus spindle speed versus humidity.

experimental formulas of exponential functions of the spindle speed.

$\Delta M_t$ = Time rate of wearing of ring (mg/hr)

$\Delta m_t$ = Time rate of wearing of traveller (mg/hr)

$\gamma$ = Wear ratio of ring and traveller, i.e., ring wearing divided by traveller wearing

$\alpha_w$ = Wear experimental coefficient, i.e., wearing in test divided by wearing in spinning

$\Delta m_c$ = Critical traveller wearing of flyout (mg)

$t$ = Life of traveller (hr)

The following experimental formulas are obtained.

$$\Delta M_t = A \cdot 10^{Bn} \tag{15}$$

$$\Delta m_t = a \cdot 10^{bn} \tag{16}$$

Hence

$$\gamma = (A/a)10^{(B-b)n} \tag{17}$$

where

$A$, $a$ = Experimental constants (mg/hr)

$B$, $b$ = Experimental constants (min/rev)

As shown in Figure 21, the amount of wearing in spinning is less than in test, but wear ratio $\gamma$ is the same in both cases. Accordingly, the law of similarity of wearing in test and in spinning holds good. Wear experimental coefficient $\alpha_w$ is high at a low speed and decreases linearly in a semilogarithmic diagram.

As shown in Figure 22, the critical wearing of flyout $\Delta m_c$ scarcely depends on spindle speed $n$, and the time rate of wearing $\Delta m_t$ increases exponentially with $n$. Therefore, the life of traveller $t$ decreases exponentially with $n$.

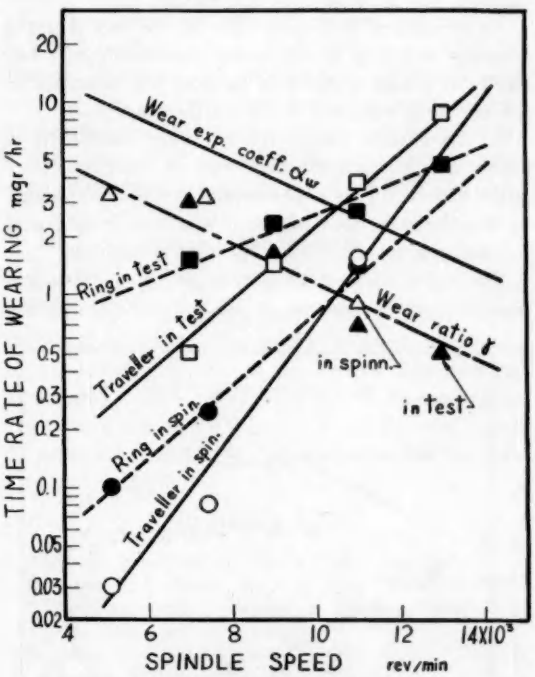



**Fig. 21.** Comparison of the wearings in spinning with those in test. (No. 1 polished ring with G-1 traveller at $12 \pm 3$°C and $75 \pm 5$% R. H.)

$$t = (\Delta m_c/a)10^{-bn} \tag{18}$$

The above-mentioned wear characteristics are applicable qualitatively to the various rings. Therefore, the experimental formulas are general. The experimental constants are given in Table IV.

*b. Wear mechanism.* According to former studies [1], the mechanism of wearing consists of three

**TABLE IV. Experimental Constants in Wear Experimental Formulas (15) and (16)**

| Ring | Humidity (% R.H.) | In Test | | | | In Spinning | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $A$ | $B$ | $a$ | $b$ | $A$ | $B$ | $a$ | $b$ |
| | 65 | $150\times10^{-2}$ | $0.00\times10^{-3}$ | $0.9\times10^{-2}$ | $0.24\times10^{-3}$ | — | — | — | — |
| No. 1. Polished | 75 | 35 | 0.09 | 2.8 | 0.19 | $1.11\times10^{-2}$ | $0.19\times10^{-3}$ | $0.089\times10^{-2}$ | $0.29\times10^{-3}$ |
| | 85 | 22 | 0.13 | 3.6 | 0.18 | — | — | — | — |
| 2. Parkerlized | 75 | 187 | 0.09 | 8.1 | 0.16 | 0.57 | 0.31 | 0.027 | 0.37 |
| 3. Granulated | 75 | 51 | 0.10 | 4.0 | 0.17 | 0.26 | 0.32 | 0.021 | 0.40 |
| 4. Nitrized | 75 | 190 | 0.05 | 4.2 | 0.20 | 1.09 | 0.23 | 0.024 | 0.38 |
| 5. U. S. A., polished | 75 | — | — | — | — | 0.60 | 0.27 | 0.018 | 0.41 |

Travellers are G-1, and rings and travellers are washed in gasoline. In spinning, 20's cotton yarn.

types, which are wearing caused by oxidation—chemical reaction in a wide sense—of surface layer, mechanical cutting and scraping, and partial welding and melting. In cast iron they are distinct from one another, but in steel they are mixed.

As mentioned in section IIB 3a, the fact that the wearing of a ring is influenced considerably by humidity at a high speed may indicate the existence of the chemical reaction of the surface layer.

In the various rings, the frictional coefficient is nearly uniform but the time rate of wearing varies fairly widely. This experimental result is explained by the characteristics of the mechanical cutting and scraping, which Bowden [2] calls "ploughing."

The worn surfaces of a ring and a traveller are nondirectionally smooth in micron order. In the experimental formulas of wearing, the time rate of wearing is not proportional to the speed but increases exponentially. This seems to explain that the partial welding and melting take place, especially at a high speed.

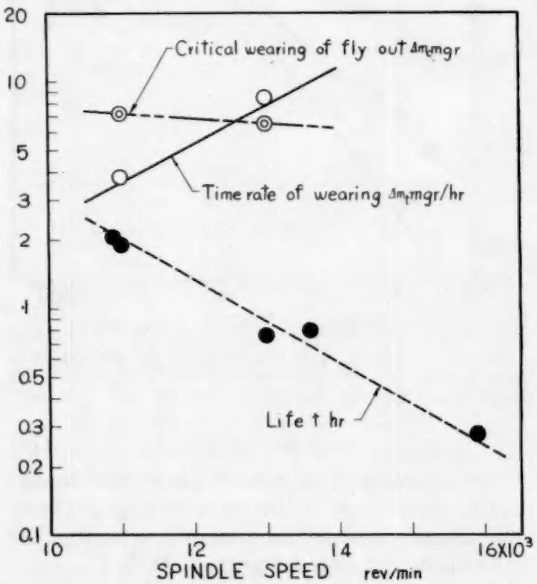



**Fig. 22.** Durability of G-1 traveller with No. 1 polished ring at 25–29°C and 85 ± 5% R. H. in test.

Generally speaking, the mechanism of wearing of a ring and a traveller may consist of (1) fragility caused by chemical reaction, (2) mechanical cutting and scraping, and (3) partial welding and melting. These elements are partially influenced by various conditions. For example, the chemical reaction is remarkable when humidity is high; so are the partial welding and melting at high speed.

### C. Summary and Conclusions

The results of static and dynamic tests of spinning rings and travellers may be summed up as follows.

The degree of circularity of spinning rings can generally be determined by measuring the diameter deviation with a dial gauge. The rings are approximately elliptic and become more so with wearing. Maximum diameter deviation is less than 0.1 mm when the ring is new and 0.05–0.3 mm when it is worn.

Hardness distribution in the section of the ring frange is measured with the Micro Vickers hardness tester. The surface layer is hard and the interior soft. In the hardened surface layer, some rings have considerably greater hardness gradient in the depth direction, and this may be one cause of wavy wearing. Surface hardness decreases with the advance of wearing and causes an increase in the amount of ring and traveller wearing. In travellers, hardness distribution is uniform in the longitudinal direction and irregular in the width.

As to the surface profiles, waviness and roughness of the contact surface, which are the envelopes by contact needles of 0.5 mm and 10 $\mu$ peak radius, are recorded on sensitive paper. Waviness of the contact

surface of a new ring is, as a rule, a sine wave having a period of one round and is superposed with irregular waves, and maximum height of the waviness is 10–40 $\mu$. As wear advances, the maximum height of waviness decreases. Some rings indicate wavy wearing after long using. The wavy wearing has a nearly constant pitch—4–7 mm, a tall wave height—0.1 mm at a maximum, and hardness difference between peak and bottom—100 V. H. at a maximum. And it is often found only on a worn ring, which has great hardness gradient in the depth direction. Therefore, wavy wearing may have a close relation with hardness gradient. Roughness of the contact surface of some new rings is directionally granular in the circumference direction. The maximum height is nearly 5 $\mu$. A new traveller has a directionally rough surface in the longitudinal direction. Worn fitted surfaces of a ring and a traveller are smooth surfaces, and their maximum height is about 1–2 $\mu$.

Frictional characteristics are measured with the self-recording type friction tester in test and in spinning and are expressed mainly by frictional force $F$ and frictional coefficient $\mu$. They are nearly similar qualitatively and quantitatively on worn fitted rings and are almost independent of the static characteristics—materials, surface treatment, etc. But they have depended remarkably on the working conditions—spindle speed, lubrication, etc. $F$ increases with spindle speed $n$, is generally proportional to the traveller weight $m$, and is expressed by experimental formulas (6), (10), and (13). $\mu$ decreases slightly with $n$, is generally independent of $m$, and is expressed by experimental formulas (8), (11), and (12).

Contact continuity $c$, which is obtained by measuring the electric current flowing through the contact resistance of a ring and a traveller, increases with $n$ and hardly depends on $m$. The fact that product $c\mu$ is nearly constant is shown by the experimental results. Hence, $\mu$ may depend mainly on $c$ only.

Lubricants reduce friction, especially at a low speed. The higher the degree of oiliness of a lubricant, the more effective it is. A lubricant, if spread, does not last long, but a porous ring permeated with a lubricant—i.e., oil-less metal—has durability. In spinning, variation of bobbin diameter changes frictional force; this is confirmed experimentally and theoretically. In an early fitting period of new rings, the friction of a nondirectional granular new ring is smaller than that of a polished directional new ring.

Wear characteristics are indicated mainly by the time rate of wearing. Those of a ring and a traveller depend somewhat on the static characteristics, materials, etc., and depend remarkably on the working conditions, especially the spindle speed and the humidity. For ring wearing, humidity is especially effective at a high speed, but for traveller it is not. These facts may be understood as an influence of the chemical reaction. The time rates of wearing of a ring and a traveller increase exponentially with the spindle speed, leading to experimental formulas (15) and (16). The traveller critical wearing of flyout is almost constant, and its life is denoted by experimental formula (18).

The mechanism of wearing of ring and traveller may be a combination of (1) fragility caused by the chemical reaction, (2) the mechanical cutting and scraping, and (3) the partial welding and melting. At a high speed, the third element may be more effective. At a high humidity, the first element may be more effective.

## Acknowledgment

This work has been done as a part of the cotton spinning research project sponsored by Japan Cotton Technical Institute. We wish to express our thanks to Mr. Julian S. Jacobs of the Textile Research Institute and to Mr. Stanley Backer of Massachusetts Institute of Technology for their critical reading of the manuscript and their cooperativeness in the publication.

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# Correlation of Laboratory Tests with Fabric Performance

## Part I: Stiffness, Puckering and Wear of Overcoat Fabrics

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**Abstract**

A basis is developed for predicting functional use characteristics of overcoat fabrics in the laboratory without going through costly, time-consuming field tests. The correlation obtained, with a representative range of fabrics, between laboratory tests and fabric performance is reviewed. The results are analyzed for significance.

### Introduction

In spite of recent scientific advances in the development of new fibers, finishes, and mechanical textile processes, final judgment of a newly developed fabric, particularly a dress fabric, still remains in the realm of empirical individual judgment and can only be verified by means of costly, time-consuming field tests. To be significant, field tests must involve the proper coordination and interpretation of many complicated physical and physiological factors. They require the use of numerous test garments and subjects; they should be carried out under a wide range of conditions; and they must be properly controlled. In addition, the evaluation and interpretation of the tests must be of sufficient scope to ascertain the presence of any unexpected complicating factor which may influence the significance of the findings. Before rapid progress can be made in the engineering of improved fabrics, new test methods must be developed to the point where reasonable predictions of service characteristics can be made in the laboratory.

As part of a Navy program of developing alternates for strategic and critical materials, numerous fabrics in new constructions and blend compositions are being procured, laboratory tested, and field evaluated. In the course of these investigations an attempt is being made to develop and verify basic engineering concepts of fabric design and performance. It is expected that as these are accomplished they will gradually reduce future dependence on extensive field evaluation and will lead to more realistic acceptance testing of the functional characteristics required in each given end-use application.

The present report is a review and analysis of correlations based on laboratory findings with representative kersey and melton overcoat fabrics and on their pertinent stiffness, puckering, and wear characteristics as encountered during recent extensive investigations [4, 5, 6].

### Discussion

Examples of puckering and wear which were found during field evaluation of the overcoats are illustrated in Figures 1 and 2. Figure 1 is a close-up view of a puckered lapel and coat front. The area from the stitching to the edge has a regularly repeating small pucker. From the stitching inward there is a more irregular larger buckling of the fabric. This incidental tailoring fault, which was more prominent with some fabrics than with others, had a marked influence on the acceptability of the test garments from an appearance viewpoint. It was found that the lighter-weight more flexible 22-oz kersey and melton fabrics gave more trouble than the present heavier and stiffer 30-oz kersey fabric. Examination showed that the puckering could have been eliminated by simple modification of the tailoring.

The useful wear life of the overcoat, as a dress item, was found to be limited by the development of threadbare areas. These were most pronounced and developed earliest at exposed folded edges of pockets, sleeves, lapels, and coat fronts. An example is shown in Figure 2, which depicts the threadbare condition of a sleeve edge. The present heavy, very stiff, 30-oz kersey fabric was found to have a relatively short wear life in comparison with the lighter-weight, more flexible, 22-oz kersey and melton fabrics.

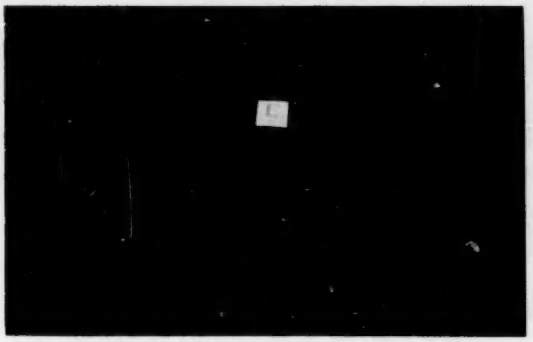

Fig. 1.

Preliminary engineering analysis indicated variations in fabric stiffness to be a primary factor contributing to the observed differences in puckering and wear. Stiffness is also a major factor influencing judgment of the feel or "hand" and the draping characteristics of a fabric. Since stiffness was found to be a common element in all phases of the present study, it will be discussed first.

*Stiffness*

Starting with Peirce [3] in 1930, numerous studies have been made of methods of measuring stiffness as a primary means of comparing the "hand" or the draping characteristics of fabrics. Emphasis in a number of recently published articles has been on the establishment of correlation between laboratory tests and subjective evaluations. In an excellent review of the commonly used test methods, carried out under the auspices of the ASTM, the cantilever method suggested by Peirce was judged to be the most significant.

A simplified cantilever stiffness tester [2] with improved accuracy has been used in numerous studies

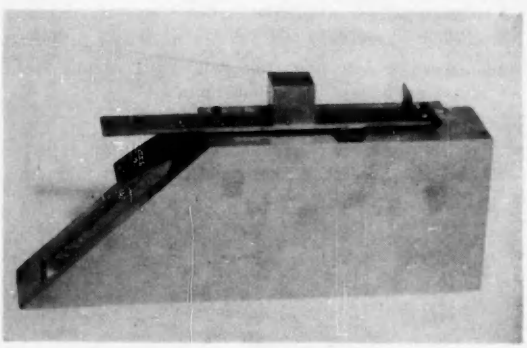

**Fig. 3a.** Drape-Flex Stiffness Tester.

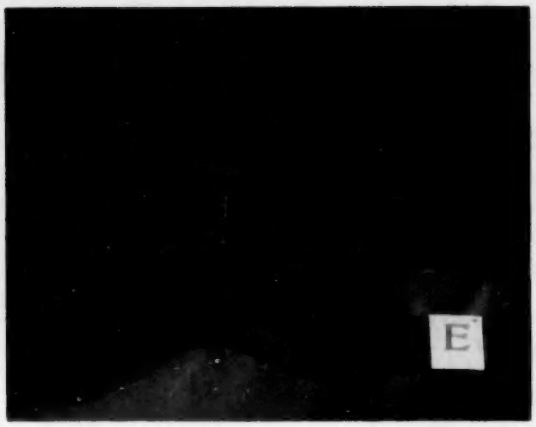

Fig. 2.

[4, 5, 6, 7] made in this office.* A picture of the instrument, known as the Drape-Flex Stiffness Tester, is shown in Figure 3*A*.

In preliminary subjective tests, 16-in. squares of the six test fabrics were ranked for stiffness by 31 qualified textile technologists. The results showed rather poor correlation with the laboratory ranking. The major irregularity appeared to be with one 22-oz fabric which in the subjective tests was surprisingly judged to be stiffer than the two 30-oz fabrics. The fabric in question was one which had a very poor finish and was very rough to the touch.

A review of the variables involved in the subjective testing indicated the desirability of reducing the size of the samples, eliminating direct contact between the hand and the fabric surface, and controlling the uniformity of the direction of flexing. The con-

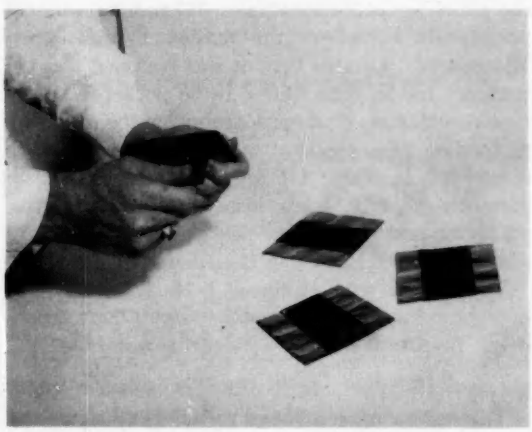

**Fig. 3b.** Stiffness testing.

ditions finally chosen for the test are illustrated in Figure 3*B*. A 4-in. square sample was covered at the two ends across the warp yarns with a 1-in. width cellophane tape. The subjects were then instructed to bend the sample up and down as shown. This gave an average value of the stiffness (flex rigidity) for face and back of the fabrics in the warp direction without direct contact with the fabric surfaces. The results of tests by 25 textile technologists are summarized and rated in Table I.

The subjective ratings are compared in Table II with average flex-rigidity values for warp bends obtained in the laboratory.

Statistical analysis of the correlation between the subjective and laboratory values in Table II yielded the following:

$$\text{Correlation Coefficient } (r) = .936$$

The correlation was judged to be highly significant since the probability of the obtained correlation being accidental is only 0.2%. Similar controlled comparative tests run with other types of fabrics have since shown a consistently high degree of correlation.

*Puckering*

Ninety enlisted men's overcoats made with the six test fabrics were field evaluated during the winter of 1951–1952. At the end of the test the garments were inspected to determine the amount of puckering and wear which had taken place. It was observed that the lapel and coat-front puckering (Figure 1) was all in the length or warpwise direction of the fabric. Examination of the interior of the stitched areas showed the puckering to be due to shrinkage of the plain woven cotton tape. When this was cut periodically to relieve the tension the puckering disappeared. On this basis it was reasoned that the tendency for an outer fabric to be puckered by the tape should be inversely proportional to the resistance to bending (flex rigidity) of the fabric in the warp direction. In Table III are listed the number of garments of each fabric which showed excessive puckering and the average flex rigidity in the warp direction as determined in the laboratory.

The inverse relationship of Table III is graphed in Figure 4 and shows a good straight-line relationship. Statistical analysis yielded the following:

$$\text{Correlation Coefficient } (r) = -.992$$

The results are considered to be highly significant with less than 3 chances in 100,000 of the correlation having been obtained by accident.

*Wear*

Observations of the wear pattern of the outer fabric in the enlisted men's overcoat showed the useful endpoint for dress wear to be the appearance of threadbare areas at exposed edges of pockets, sleeves, lapels, and coat fronts (see Figure 2). Engineering analysis indicated the major components of the accelerated surface edge wear to be the durability of the cover or nap and the stiffness of the fabric.

An early report [7] from this office pointed out the need for suitable methods to test the surface-appearance retention characteristics of fabrics. In a later report [4] a review was made of the principal deficiencies of currently available abrasion equipment for measuring surface durability characteristics. In the same report a structural analysis was made of the surface durability deficiencies of the 30-oz kersey. In addition, the engineering of new 22-oz fabrics with improved surface durability was discussed, and durability results with a new appearance-retention tester were presented. The tester combines the following essential features: (a) uniform controlled mounting of the samples; (b) minimum sample tension; (c) a mild abradant which acts on the surface of the fabric only; (d) low contact pressure; and (e) a circular reciprocating motion. Cotton duck was used as the abradant with a contact pressure of 0.05 psi.

**TABLE I. Subjective Stiffness**

| Fabric | | Increasing Stiffness Ranking* | | | | | | Subjective |
|---|---|---|---|---|---|---|---|---|
| No. | Type | 1 | 2 | 3 | 4 | 5 | 6 | Rating† |
| K9 | 22-oz kersey | 9 | 11 | 4 | 1 | | | 47 |
| K6 | 22-oz kersey | 8 | 10 | 7 | | | | 49 |
| M2A | 22-oz melton | 8 | 4 | 12 | 1 | | | 56 |
| M4A | 22-oz melton | | | 2 | 23 | | | 98 |
| K7 | 30-oz kersey | | | | | 19 | 6 | 131 |
| K8 | 30-oz kersey | | | | | 6 | 19 | 144 |

* Summary of individual rankings.
† Sum of products of individuals times rankings.

**TABLE II. Subjective Rating and Laboratory Stiffness**

| Fabric | Subjective Rating | Flex Rigidity* ($\times 10^{-4}$ in.-lb) |
|---|---|---|
| K9 | 47 | 4.9 |
| K6 | 49 | 5.1 |
| M2A | 56 | 4.9 |
| M4A | 98 | 6.4 |
| K7 | 131 | 14.2 |
| K8 | 144 | 17.7 |

* See Reference 2 for details of test method.

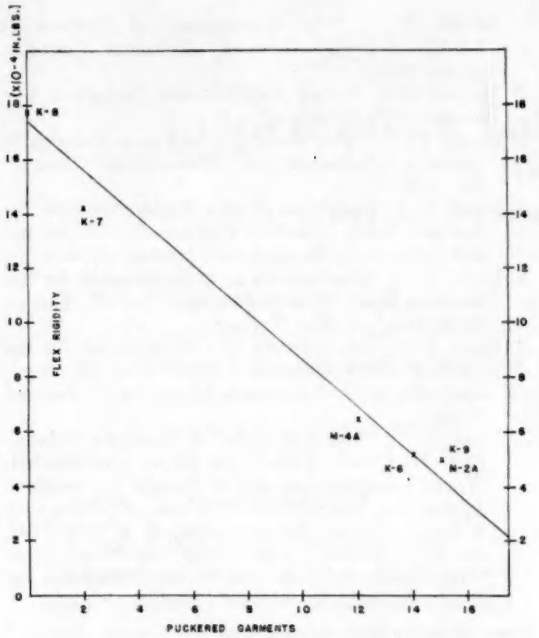


**Fig. 4.** Puckering vs. flex rigidity.

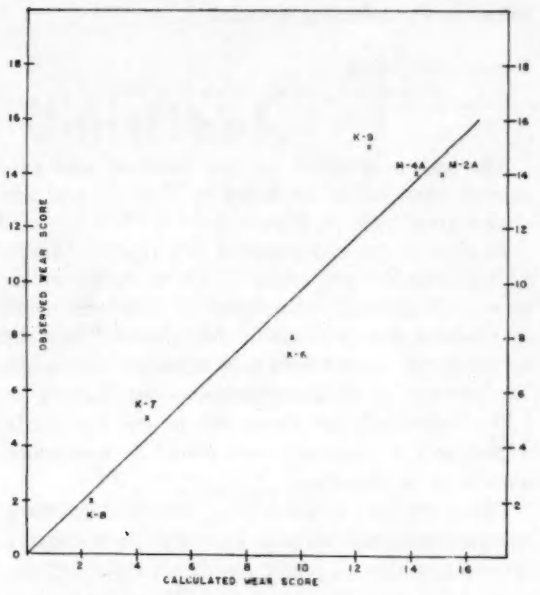


**Fig. 5.** Observed vs. calculated wear score.

Measurement of change in thickness was made periodically. At the same time the number of cycles required to wear off sufficient surface cover to make the fabric threadbare was determined visually.

In Table IV are combined the factors which were finally chosen for correlation. For the stiffness (flex rigidity) values, the geometric mean of the face-up test in the warp and filling directions was used.

The observed wear score as compared with the abrasion-cycle and flex-rigidity data shows a correlation coefficient as follows:

Multiple Correlation Coefficient $(r_{a \cdot bc}) = .964$

This correlation is considered to be highly significant, involving less than a 0.3% possibility of coincidence. This high degree of correlation indicates that abrasion-cycle and flex-rigidity data may be used to obtain a satisfactory wear-score index without the necessity of undergoing extensive service tests.

Calculation of the Least-Squares Regression Plane

**TABLE III. Puckering and Stiffness**

| Fabric | Type | Puckered Garments | Flex Rigidity* |
|---|---|---|---|
| K8 | 30-oz kersey | 0 | 17.7 |
| K7 | 30-oz kersey | 2 | 14.2 |
| M4A | 22-oz melton | 12 | 6.4 |
| K6 | 22-oz kersey | 14 | 5.1 |
| M2A | 22-oz melton | 15 | 4.9 |
| K9 | 22-oz kersey | 15 | 4.9 |

* For test method see Reference 2.

**TABLE IV. Wear Factors**

| Fabric No. | Type | Observed Wear Score* | Abrasion Cycles† | Flex Rigidity* |
|---|---|---|---|---|
| K8 | 30-oz kersey | 2 | 6,000 | 17 |
| K7 | 30-oz kersey | 5 | 6,000 | 14 |
| K6 | 22-oz kersey | 8 | 2,500 | 5.1 |
| K9 | 22-oz kersey | 15 | 10,000 | 4.6 |
| M4A | 22-oz melton | 14 | 20,000 | 6.6 |
| M2A | 22-oz melton | 14 | 20,000 | 5.2 |

* Number of garments cut of 15 issued which did not show excessive wear.

† Press—CSO Appearance Retention Tester. Cycles required to wear off surface cover or nap.

‡ According to CCC-T-191b, Method 5206.

**TABLE V. Observed and Calculated Wear Scores**

| Fabric No. | Type | Observed Wear Score | Calculated Wear Score |
|---|---|---|---|
| K8 | 30-oz kersey | 2 | 2.3 |
| K7 | 30-oz kersey | 5 | 4.4 |
| K6 | 22-oz kersey | 8 | 9.7 |
| K9 | 22-oz kersey | 15 | 12.4 |
| M4A | 22-oz melton | 14 | 14.1 |
| M2A | 22-oz kersey | 14 | 15.1 |

for the purpose of estimating wear-score indices resulted in the following equation:

$$\text{Wear-Score Index} = \frac{\text{Abrasion Cycles}}{3195} - \frac{\text{Flex Rigidity}}{1.404} + 12.535$$

The values obtained for the observed and calculated wear scores are listed in Table V and are shown graphically in Figure 5.

In view of the wide range of flex rigidity (4.6 to $17 \times 10^{-4}$ in-lb) and cover (2,500 to 20,000 cycles to wear off the nap) represented by the present overcoat fabrics, the closeness of the calculated and observed scores is considered to be definitely significant. The standard error of estimate was calculated to be 1.34. Statistically this means that in over two-thirds of the cases, a variation of less than 1.34 wear-score units is to be expected.

These results indicate that simple laboratory measurements can be used by means of a suitably derived equation to predict, with a satisfactory degree of accuracy, the useful wear life of kersey and melton overcoat fabrics.

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*Manuscript received March 10, 1955.*


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